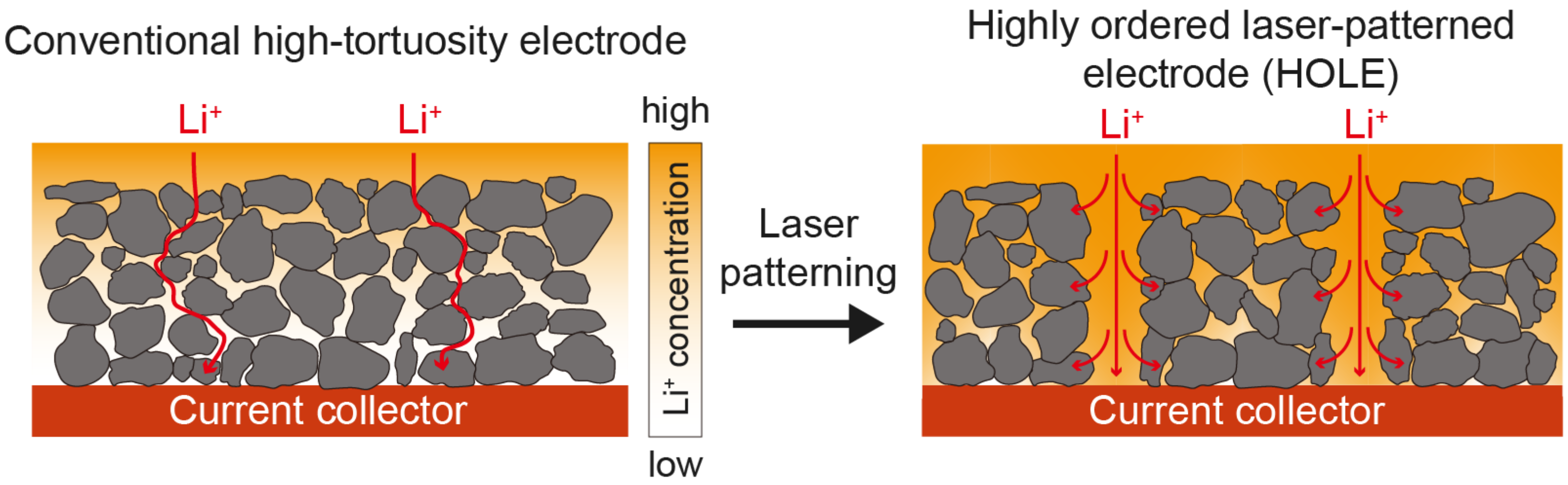
MICHIGAN ENGINEERING
UNIVERSITY OF MICHIGAN

Highly Ordered Hierarchical Anodes for Extreme Fast-Charging Batteries



PI: Neil P. Dasgupta

University of Michigan, Ann Arbor

DOE Vehicle Technologies Program Annual Merit Review

June 1-4, 2020

bat394

Overview

Timeline

- Project start date: July 1, 2018
- Project end date: August 31, 2020
- Percent complete: 88%

Budget

- Total project funding: 1,667k
  - DOE share: 90%
  - Contractor share: 10%
- Funding for FY 2018: $883k
- Funding for FY 2019: $784k
- Funding for FY 2020: $0

Barriers

- Barriers addressed
  - Extreme fast charging of batteries with energy density > 180 Wh/kg
  - Cycle life and durability of cells
  - 3-D electrode design

Partners

- Principal Investigators
  - Neil Dasgupta, Jeff Sakamoto, Katsuyo Thornton, Jyoti Mazumder (University of Michigan)
  - Mohan Karulkar (Sandia National Lab)
- Collaborators
  - Andrew Jansen, Venkat Srinivasan (ANL)
  - Mike Toney (SLAC)
  - Vanessa Wood (ETH Zürich)
  - Joshua Lamb, Loraine Torres-Castro (Sandia)

Relevance

Objective

- Demonstrate >2 Ah pouch cells with an energy density > 180 Wh/kg, capable of a 10-minute fast charge protocol, and 500 cycles with < 20% fade in specific energy

Relevance

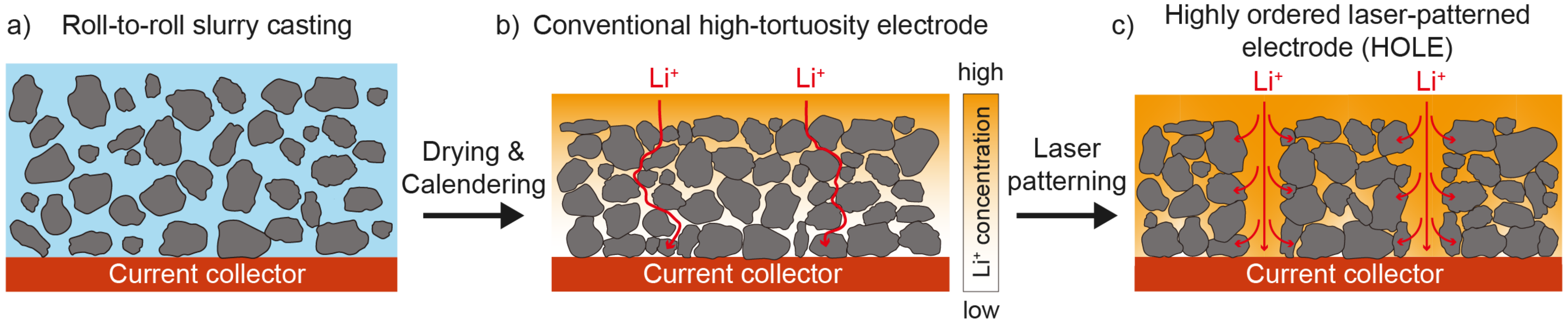
- Overcome tradeoff between energy density and power density
- Demonstrate a scalable pathway for electrode modification that is directly compatible with existing roll-to-roll manufacturing
- Experimentally-informed modeling to optimize 3-D electrode architectures
- Improved fundamental understanding of Li plating through advanced metrology/characterization

Impact

- Enable 10-min charging without significantly impacting energy density or manufacturing cost
- Accelerate public acceptance of EVs by reducing range anxiety and making re-charging competitive with refueling of internal combustion engines

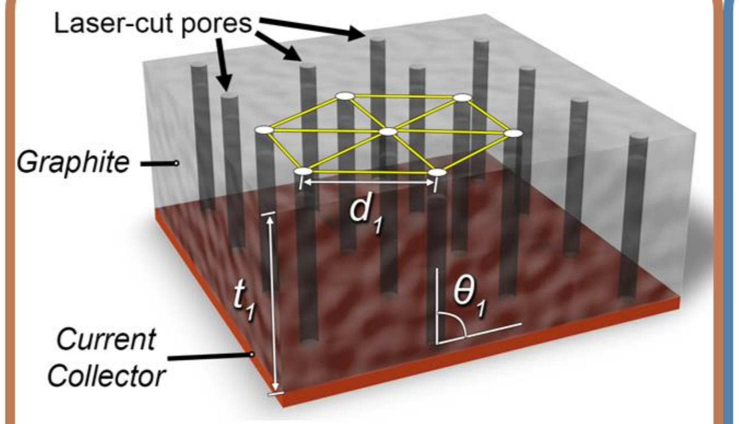
Approach

- <u>Highly ordered laser-patterned electrodes (HOLE) design</u>
- Perform laser patterning to engineer pore channels into post-calendered graphite anodes
- Pore channels facilitate ionic flow
  - Reduced concentration gradients / cell polarizations
  - Improved accessible capacity and minimized Li plating



Approach

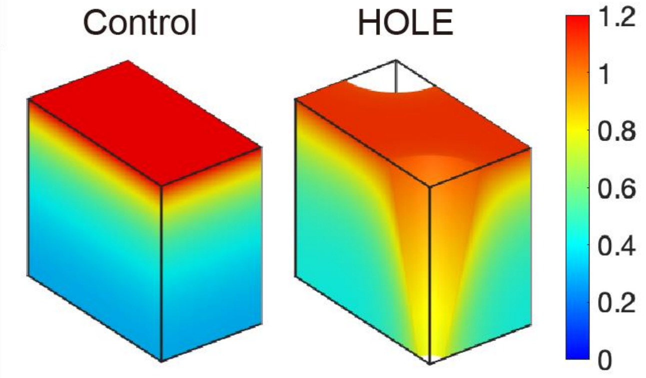
- Technical approach including main tasks, PI expertise, and key experimental techniques



Design and Manufacturing

PIs: Dasgupta, Sakamoto, Mazumder

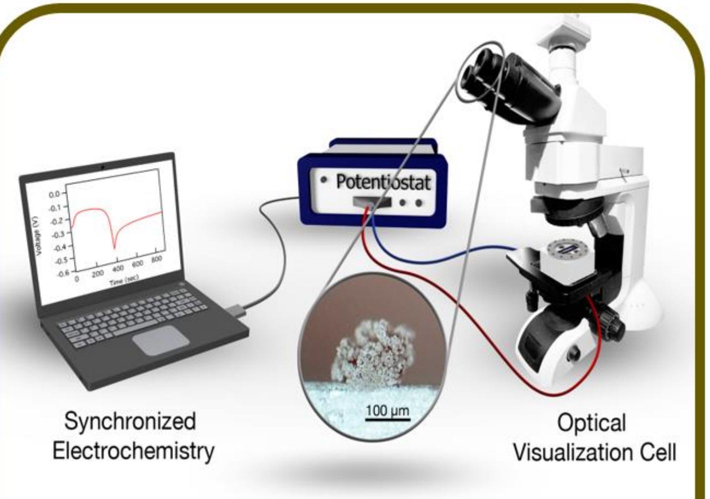
1. Design of HOH architecture
2. Laser manufacturing
3. Interface modification (ALD)
4. Scale up and automation of cell manufacturing



Computational modeling

PI: Thornton

1. Effect of porosity and tortuosity on transport
2. Hierarchical geometry
3. Electrolyte concentration and temperature dependence



Operando characterization

PIs: Dasgupta, Karulkar

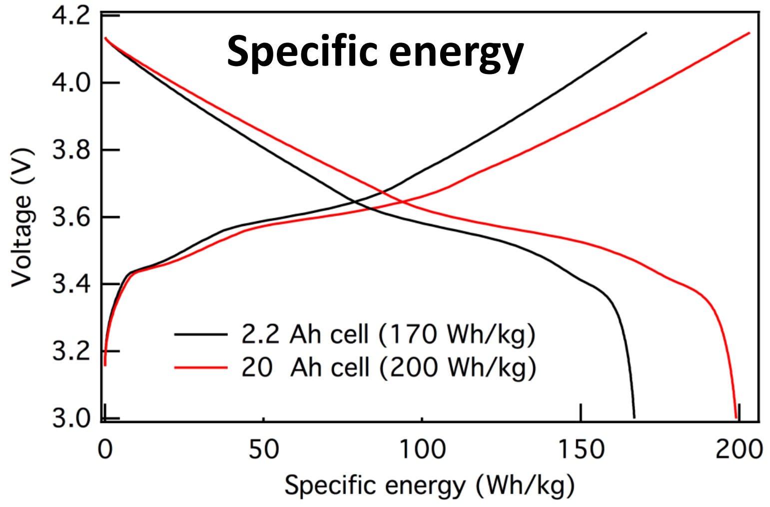
1. Operado microscopy and spectroscopy of Li plating
2. High-precision Coulometry
3. Rapid EIS

Approach - milestones

Month/Year	Type	Description of Milestone	Status
Aug. 2019	MS	Generate *operando* video microscopy data for HOLE anodes for varying current densities	**Complete**
Aug. 2019	GO/NG	Deliver 9 cells of > 2 Ah capacity and demonstrate 200% improvement in capacity retention over 100 cycles at 4C rate and 100% improvements at 6C rate	**Complete**
Nov. 2019	MS	Demonstrate ALD fast ion conductor on graphite anodes with tunable thickness and cycle at varying C-rates	**Complete**
Feb. 2020	MS	Simulate a charge/discharge cycle for a HOLE half-cell and predict concentration gradients as a function of pore diameter and spacing	**Complete**
May 2020	MS	Use HPC and Rapid EIS to generate early Li plating markers in cycling efficiency, voltage, dQ/dV, and impedance during XFC	On schedule
Aug. 2020	MS	Confocal Raman scans of HOLE anodes for current densities ranging from 1-10 mA/cm^2	On schedule
Aug. 2020	D	Deliver 18 cells of > 2 Ah capacity capable of delivering > 180 Wh/kg at the beginning of life and > 144 Wh/kg (< 20% capacity fade) after 500 cycles of 6C/1C charge/discharge	On schedule

Accomplishment - pouch cell fabrication

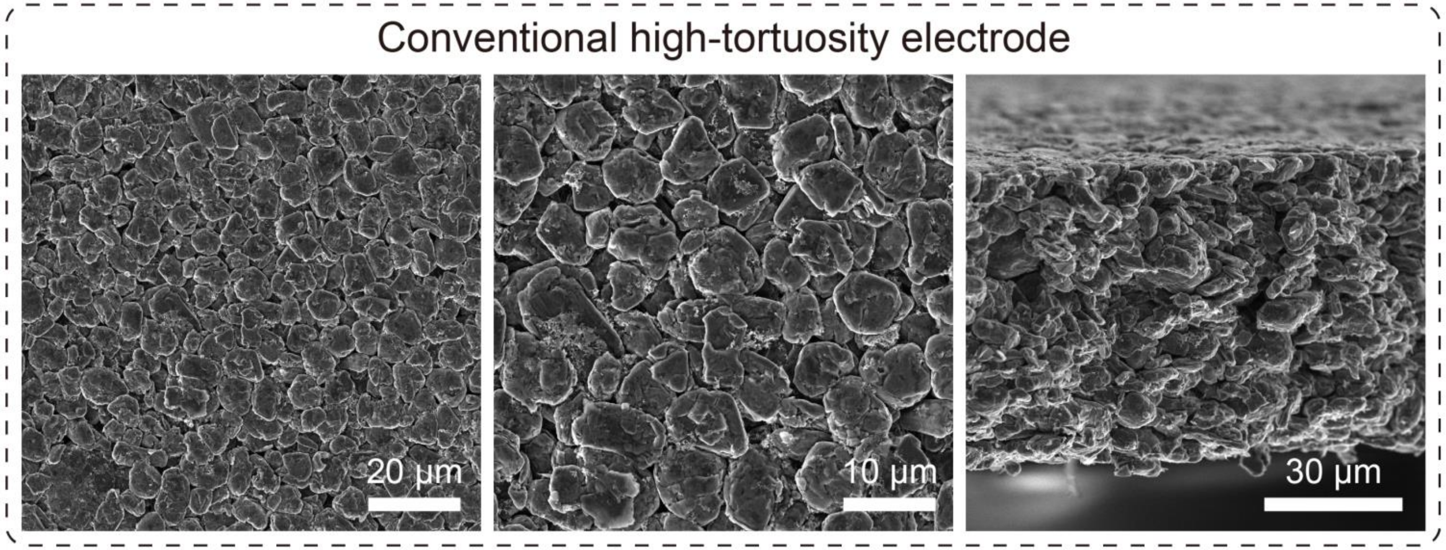
- Fabricate graphite-NMC pouch cells (> 2 Ah multi-layer cells)
  - 2.2 Ah cells (170 Wh/kg) and 20 Ah cells (200 Wh/kg)
- Industrially relevant electrode conditions (> 3 mAh/cm^2 graphite anode)
- U-M battery laboratory: pilot-scale roll-to-roll processing



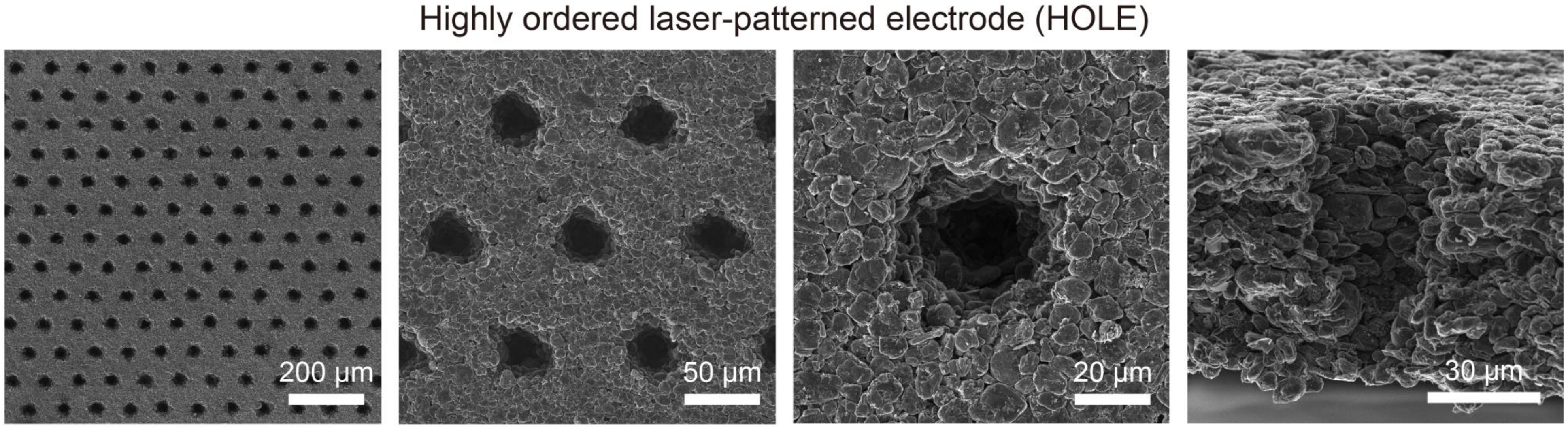
Electrode fabrication room

Cell assembly dry room

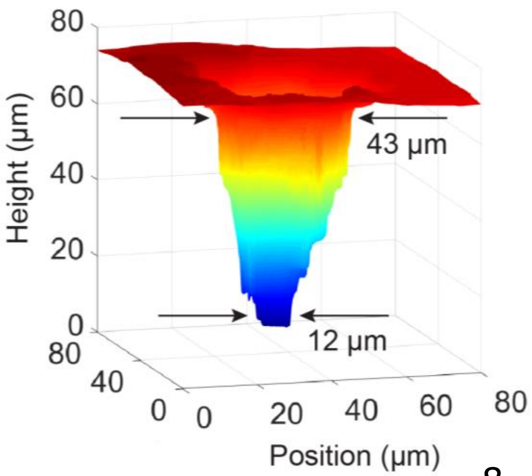
Accomplishment - electrode morphology



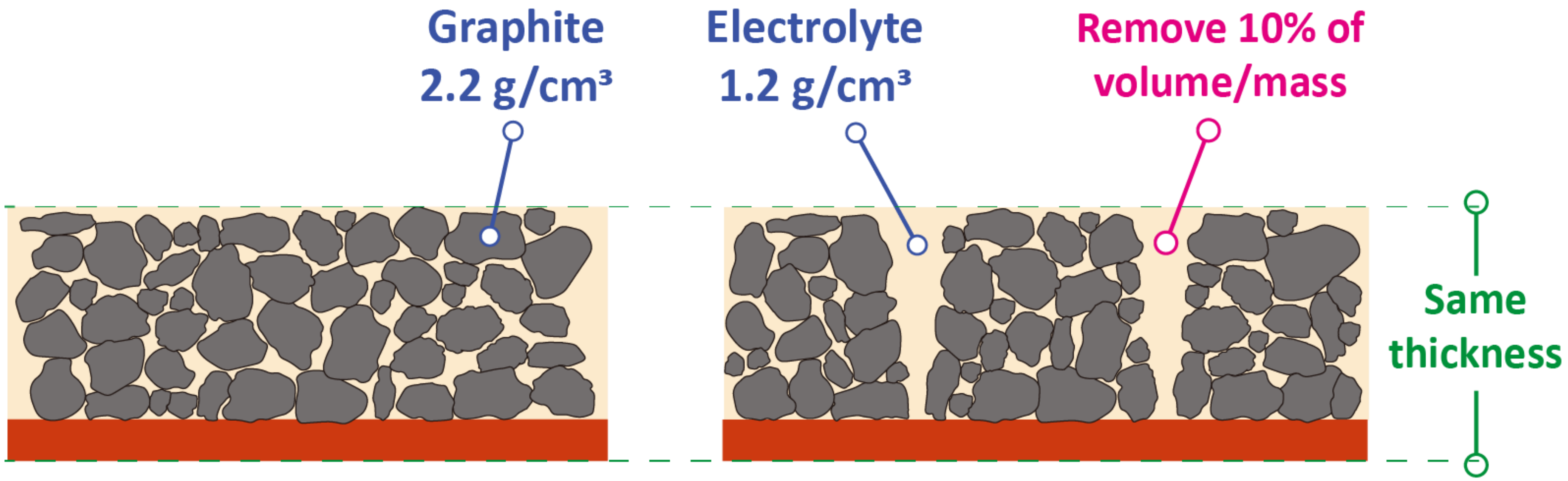
- <u>Graphite anode details</u>
  - 9.48 mg/cm^2 mass loading
  - 3.2 mAh/cm^2 areal capacity
  - 1.44 g/cm^3 tap density
  - 32% porosity



Laser patterning removed ~10% material



Accomplishment - electrode morphology



Control

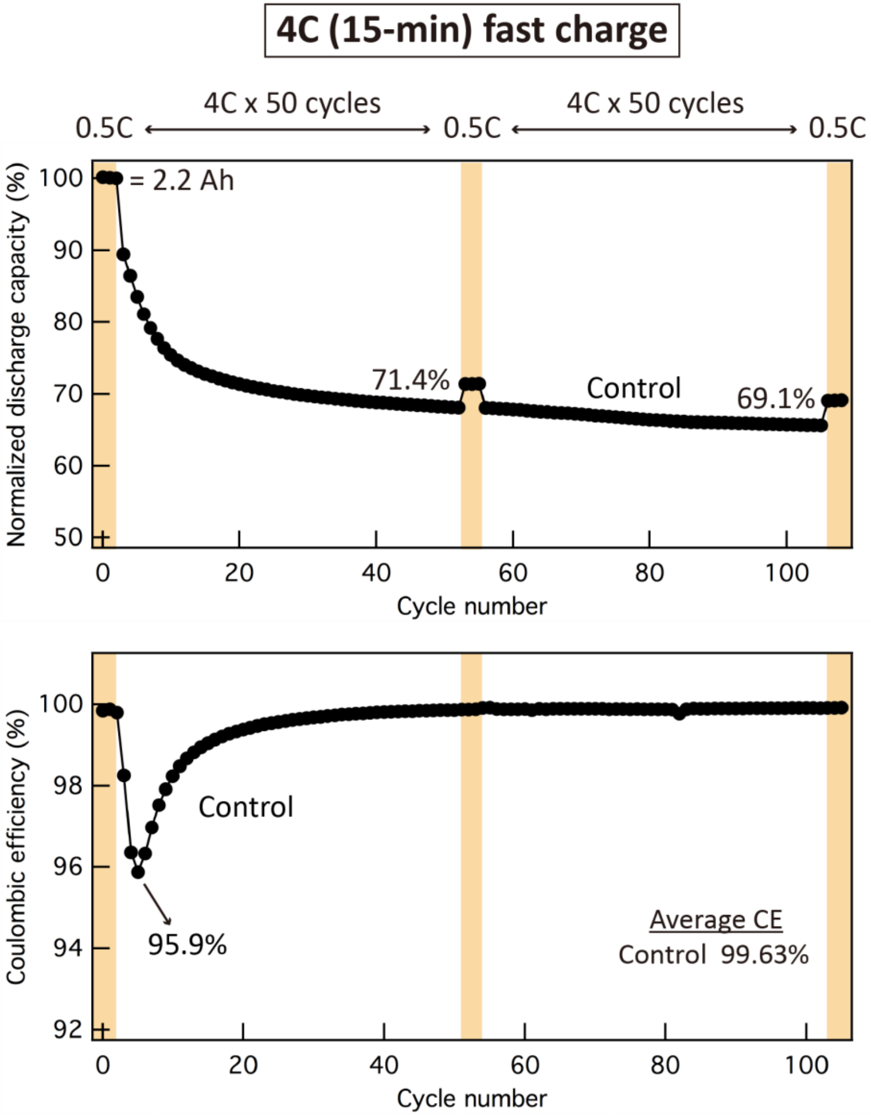
- 3.2 mAh/cm² anode
- 2.6 mAh/cm² cathode
- N/P ratio = 1.23

HOLE

- 2.9 mAh/cm² anode
- 2.6 mAh/cm² cathode
- N/P ratio = 1.11
- Same Wh/L
- Higher Wh/kg

Accomplishment - fast-charge cycling

- Demonstrated improved capacity retention during fast charging (Go/No Go milestone, Aug. 2019)



Accomplishment - fast-charge cycling

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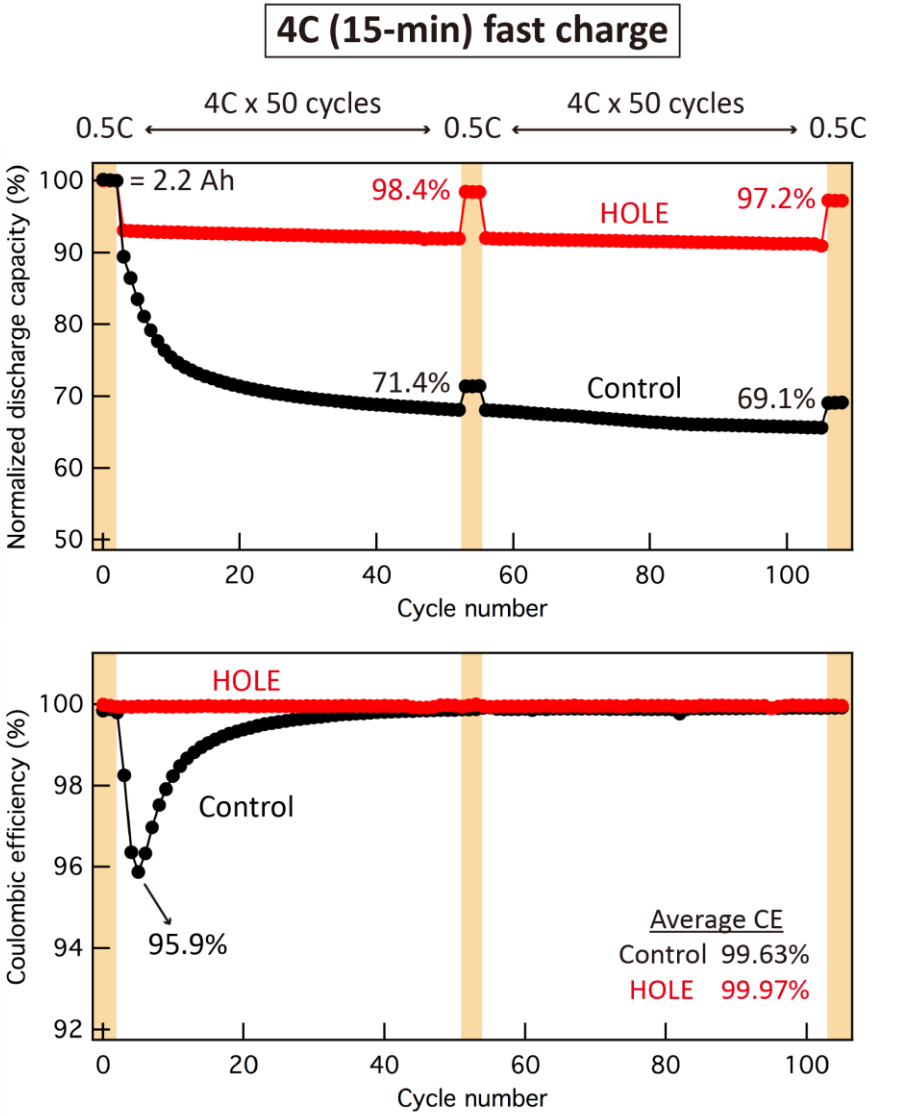

Accomplishment - fast-charge cycling

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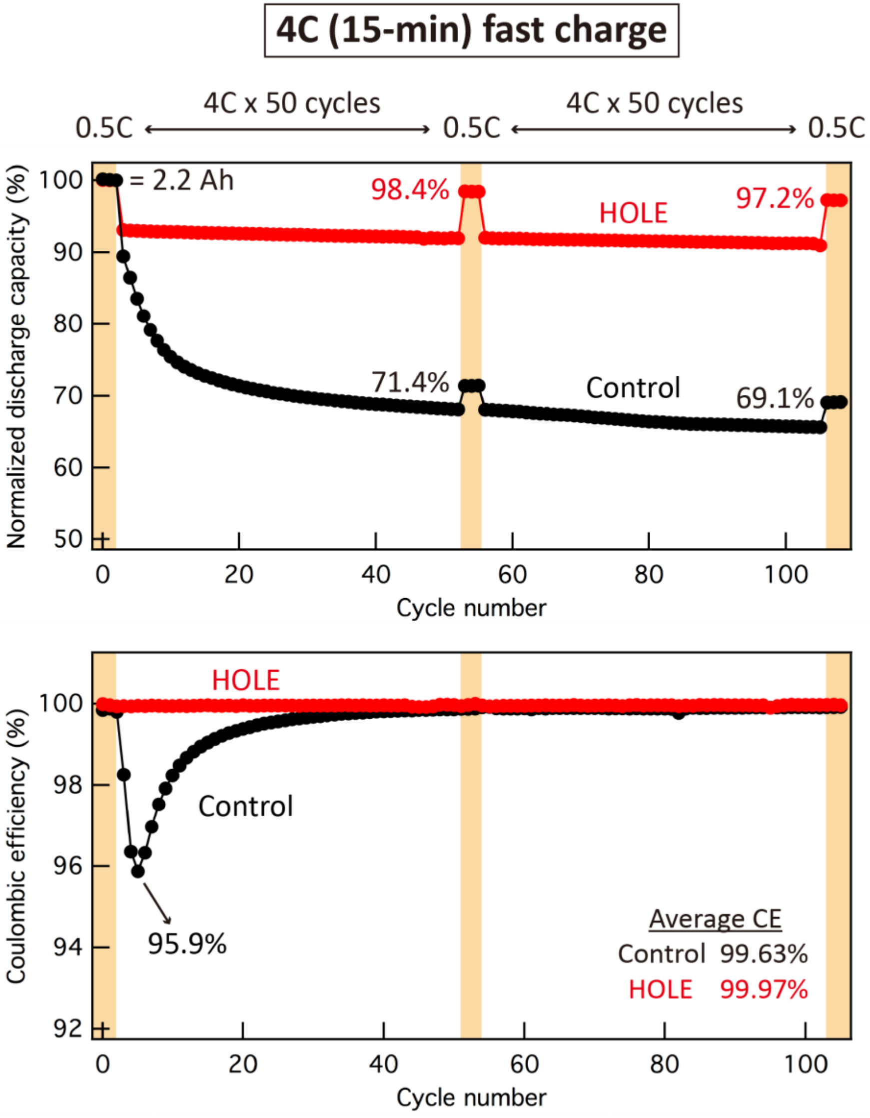
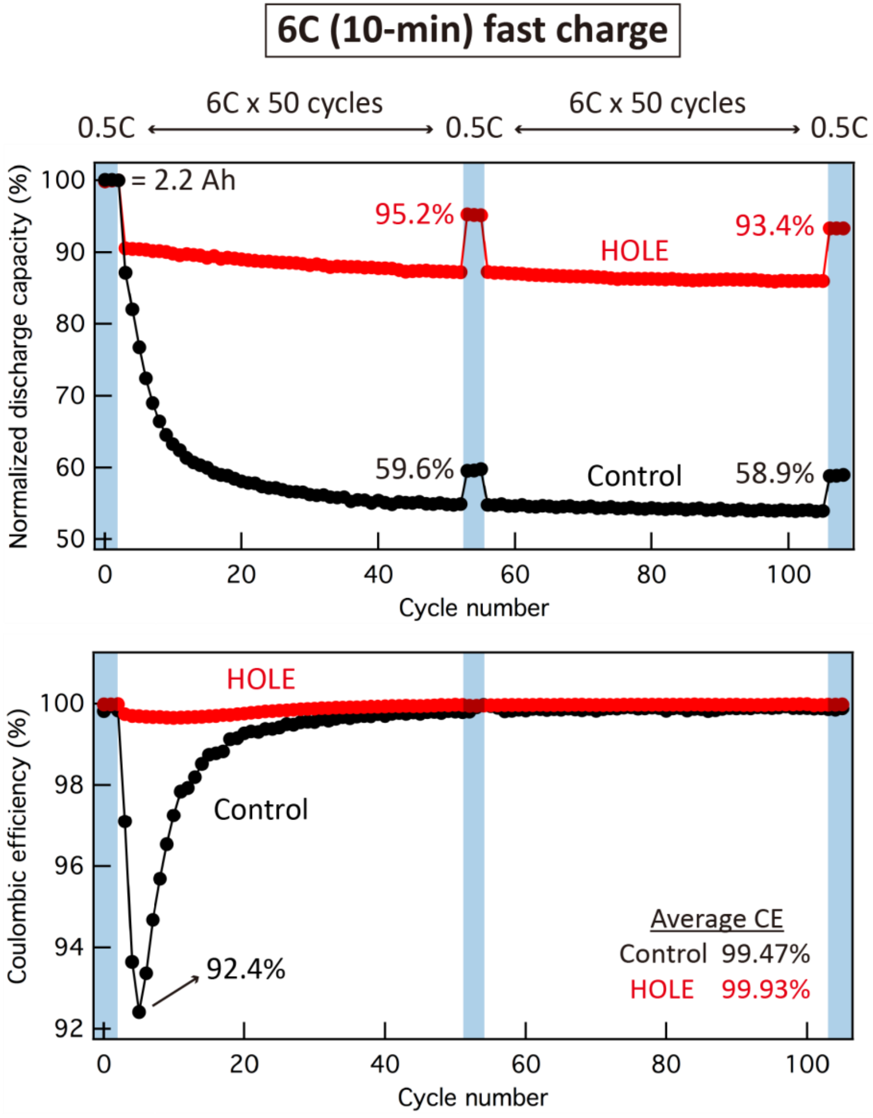
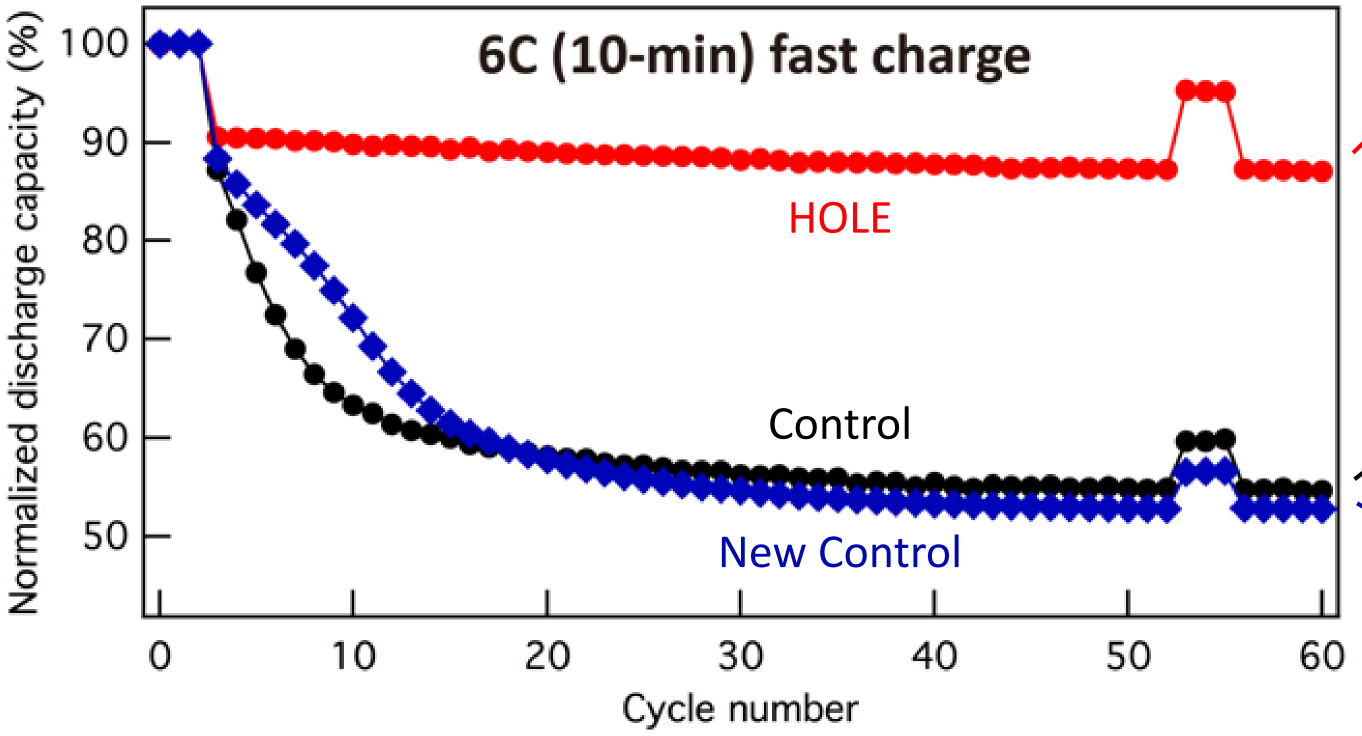
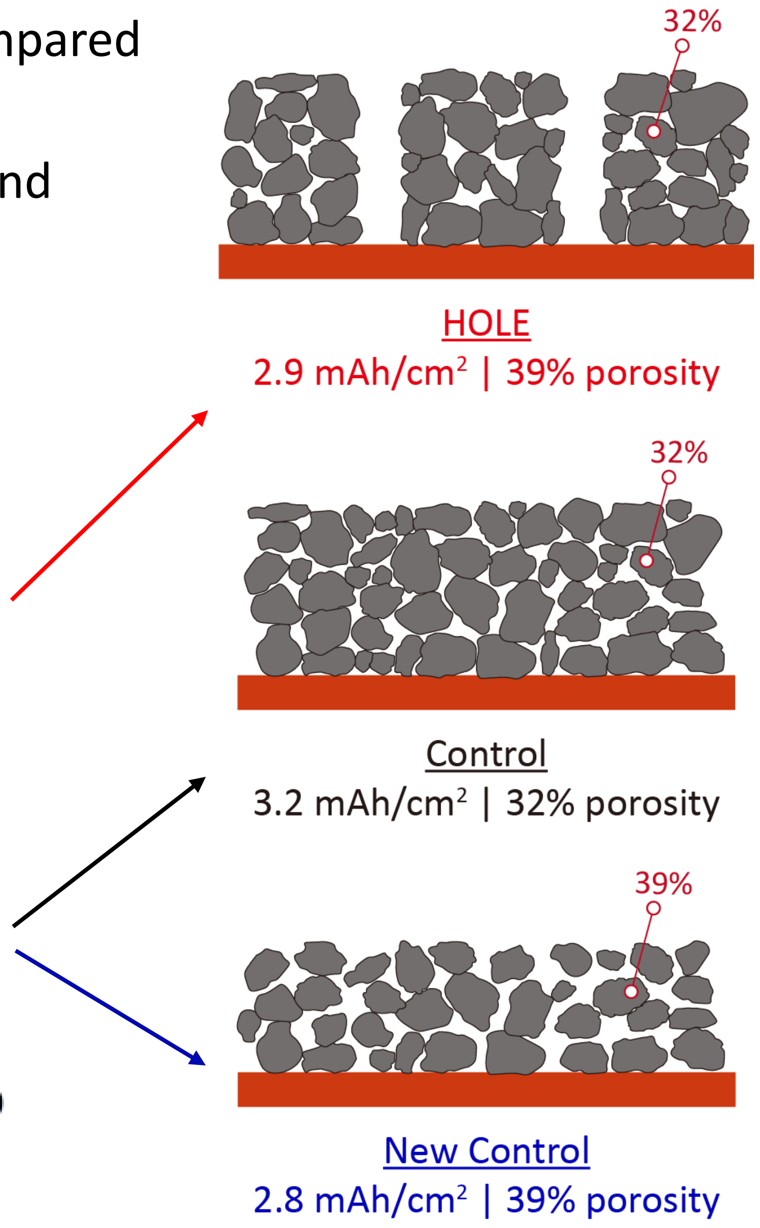




Accomplishment - demonstrate advantage of 3-D structure

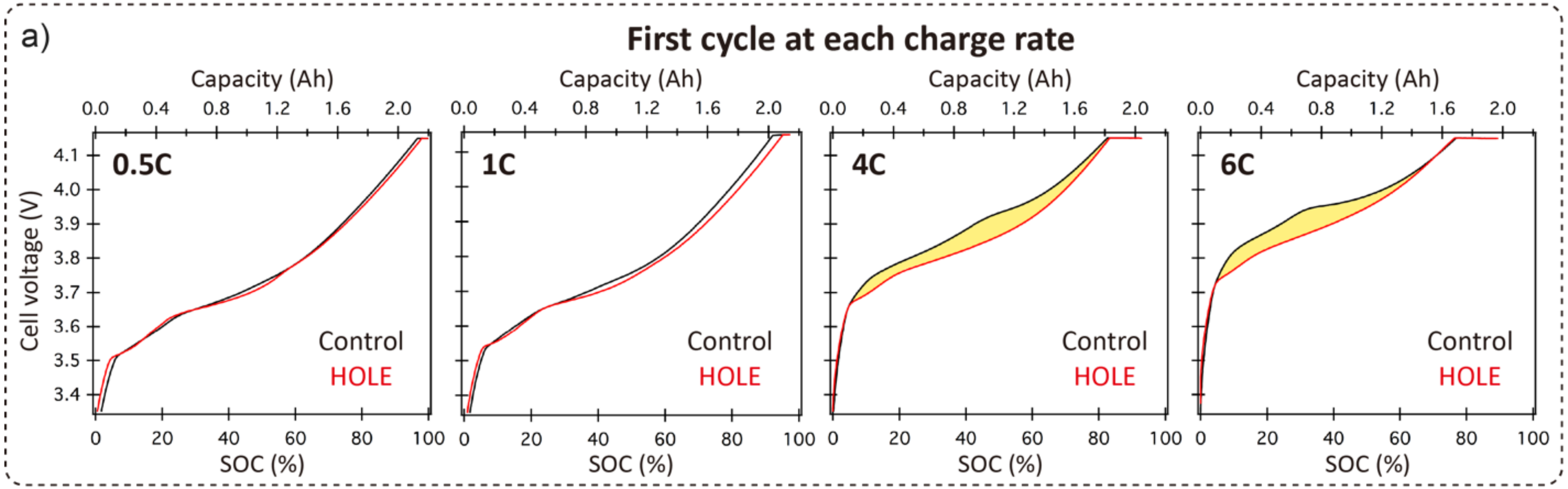
- HOLE anodes have a lower loading and higher total porosity compared to control
- Similar capacity fade observed regardless of the lower loading and higher porosity conventional anode
- Demonstrate the importance of through-plane ionic transport





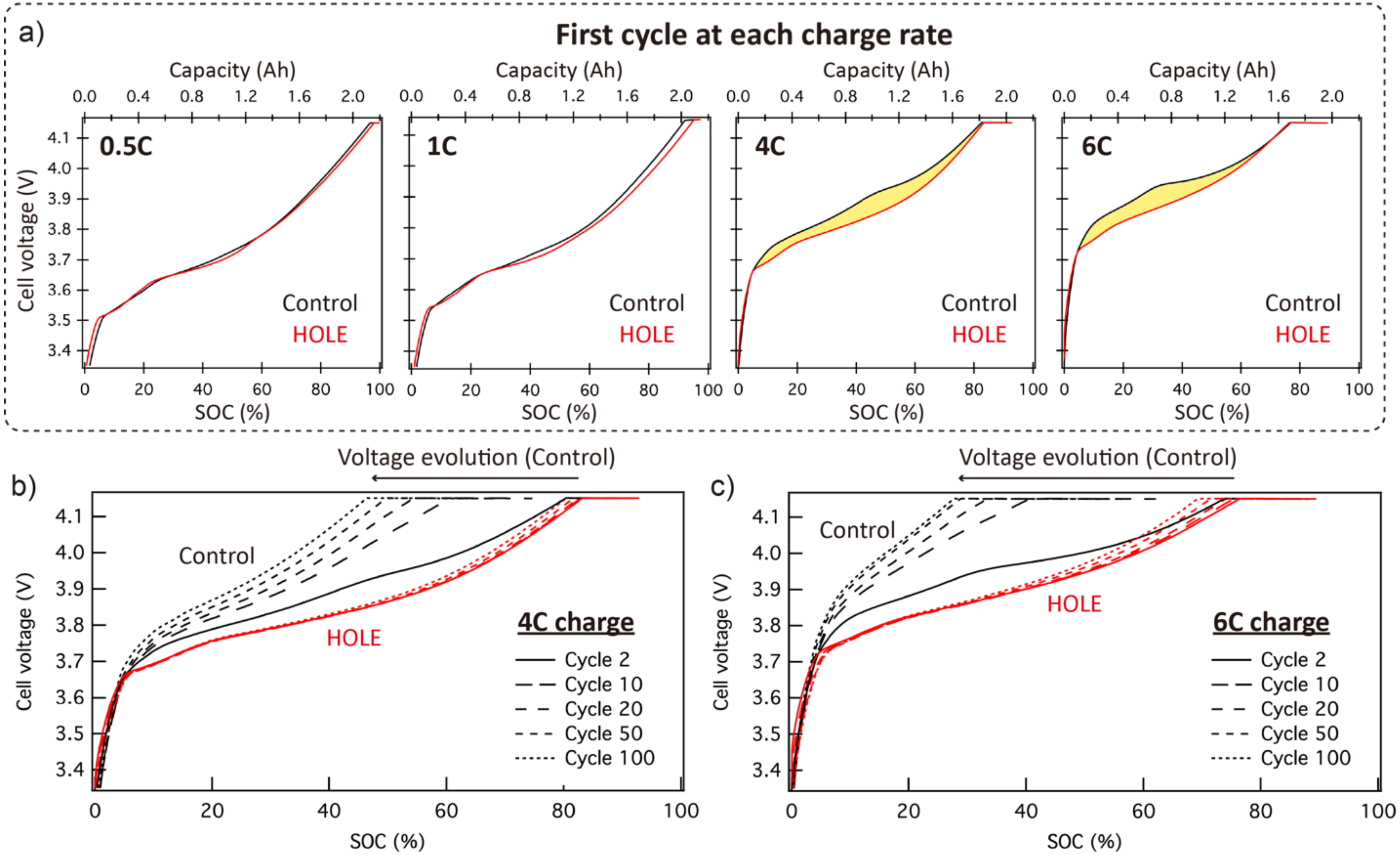
Accomplishment - voltage analysis

- Stable voltage evolution and reduced cell polarizations of HOLE cells compared to Control cells



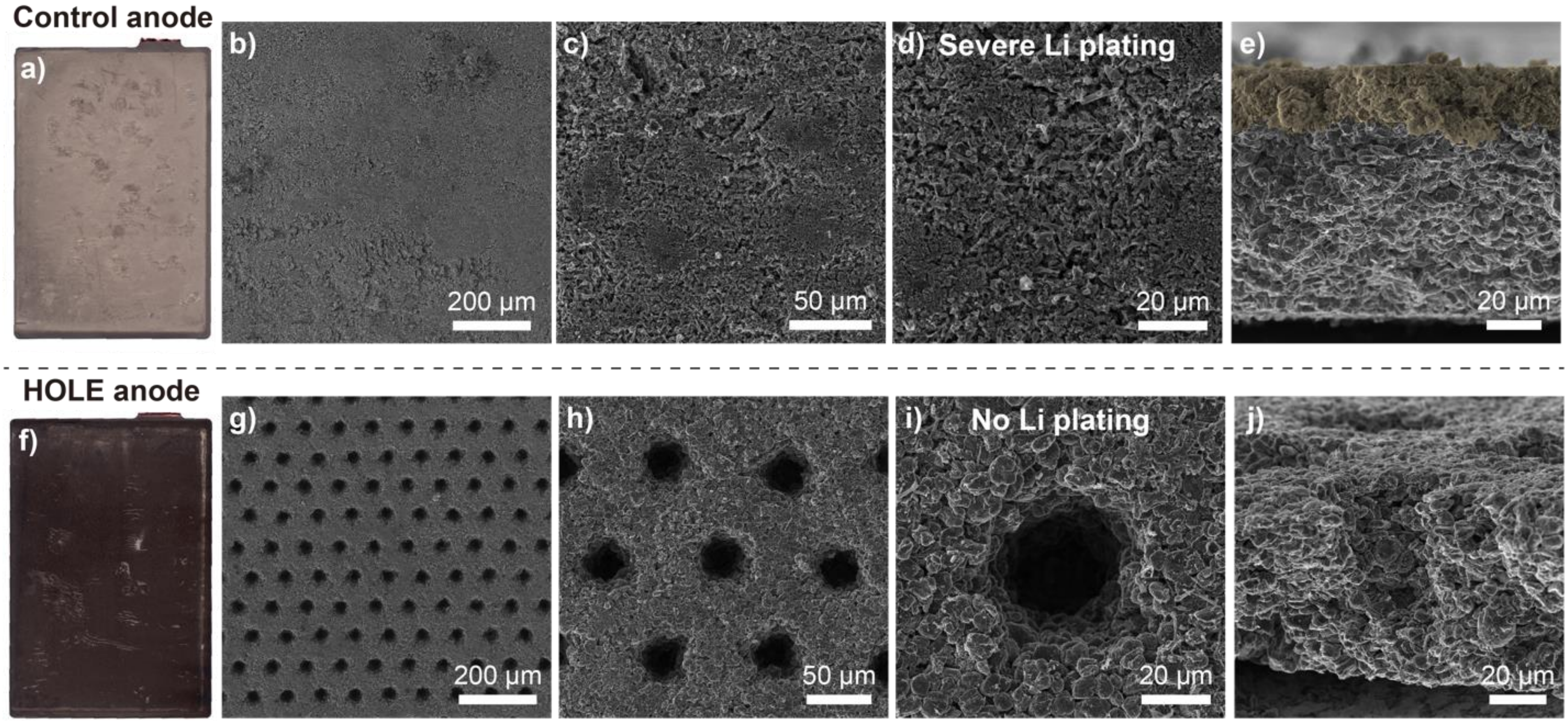
Accomplishment - voltage analysis

- Stable voltage evolution and reduced cell polarizations of HOLE cells compared to Control cells



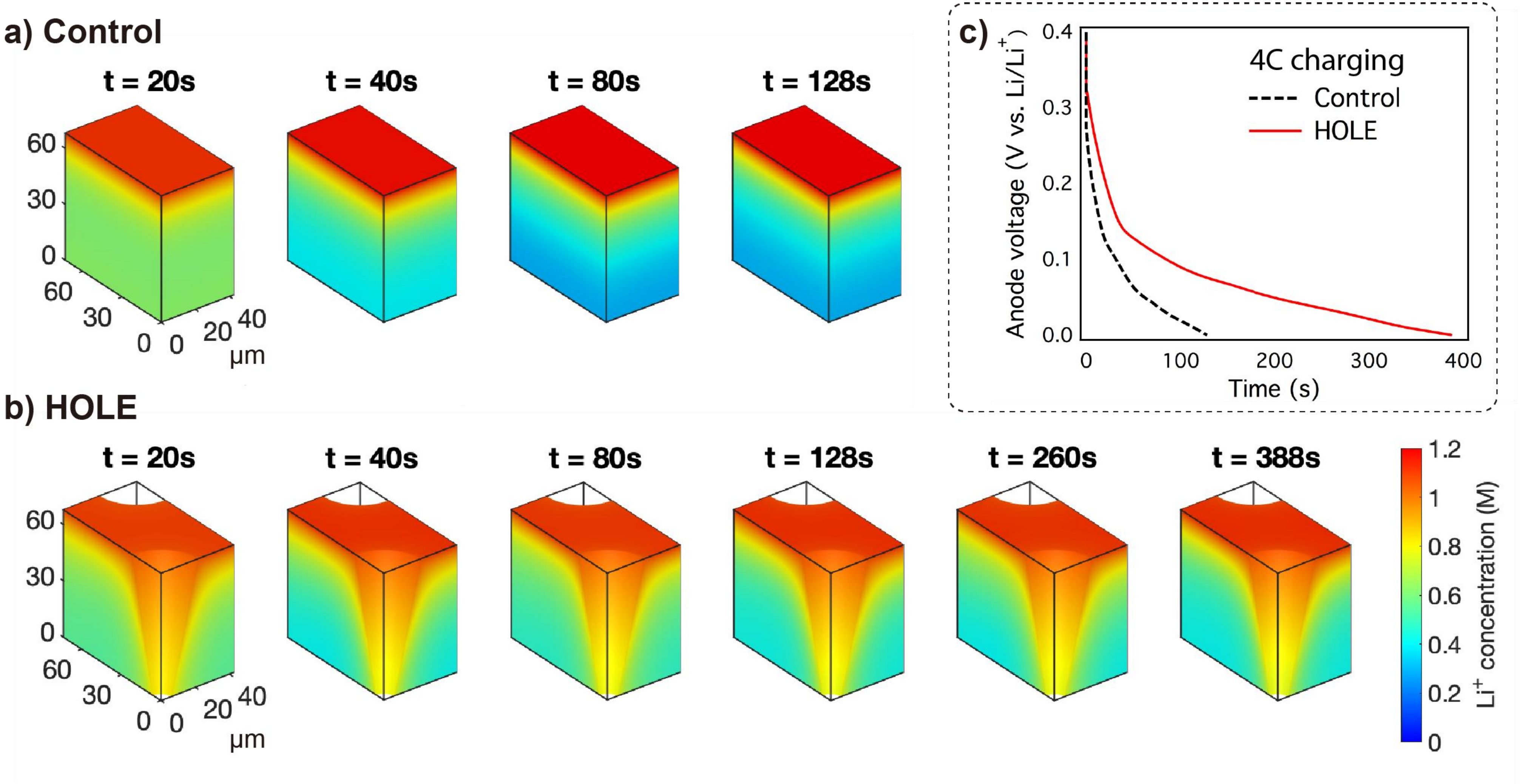
Accomplishment - post-mortem analysis

- Pouch cell teardown after XFC cycling showing the degree of Li plating on pouch cells



Accomplishment - electrochemical simulations

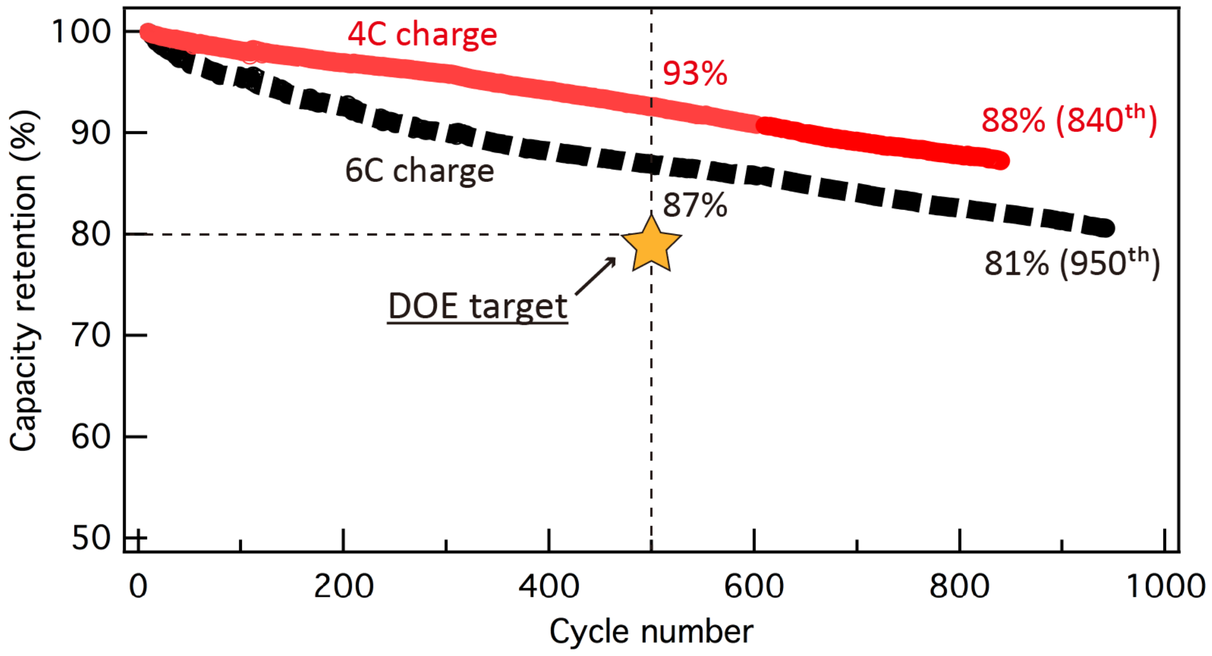
- Simulated voltage profiles of Control and HOLE anodes during fast charging and predict concentration gradients (Milestone, Feb. 2020)



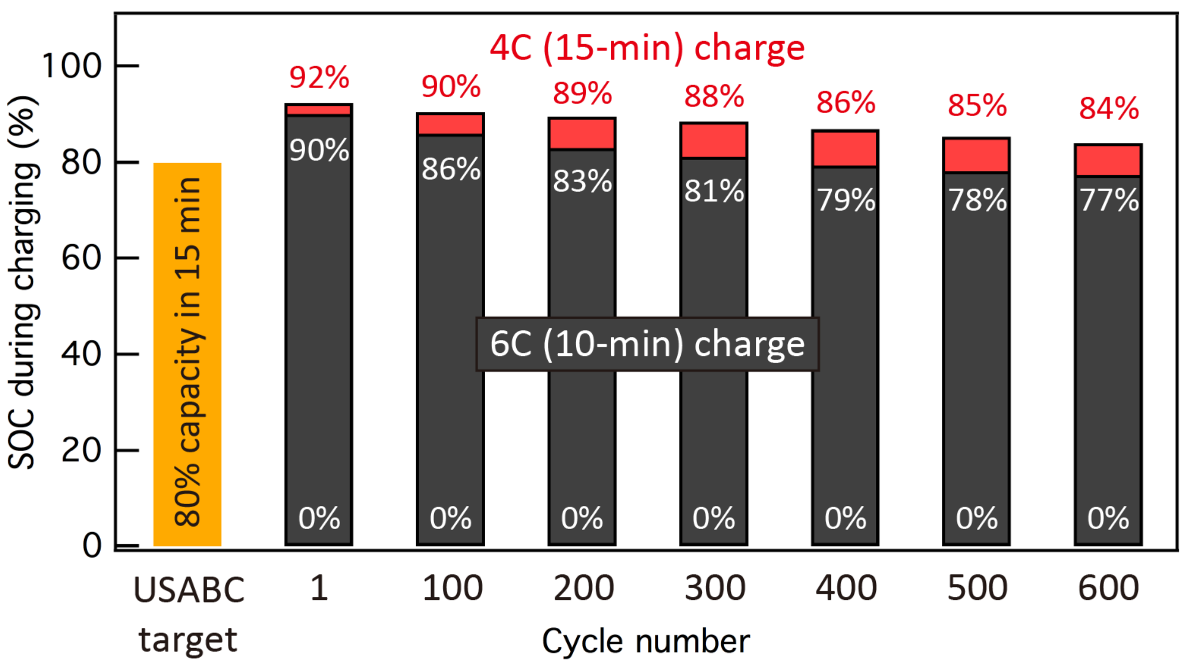
Accomplishment - long-term cycling

- Demonstrated > 2 Ah cells capable of delivering > 180 Wh/kg and < 20% capacity fade after 500 cycles of 6C fast charging (Milestone, Aug. 2020 – on schedule)

DOE XFC target

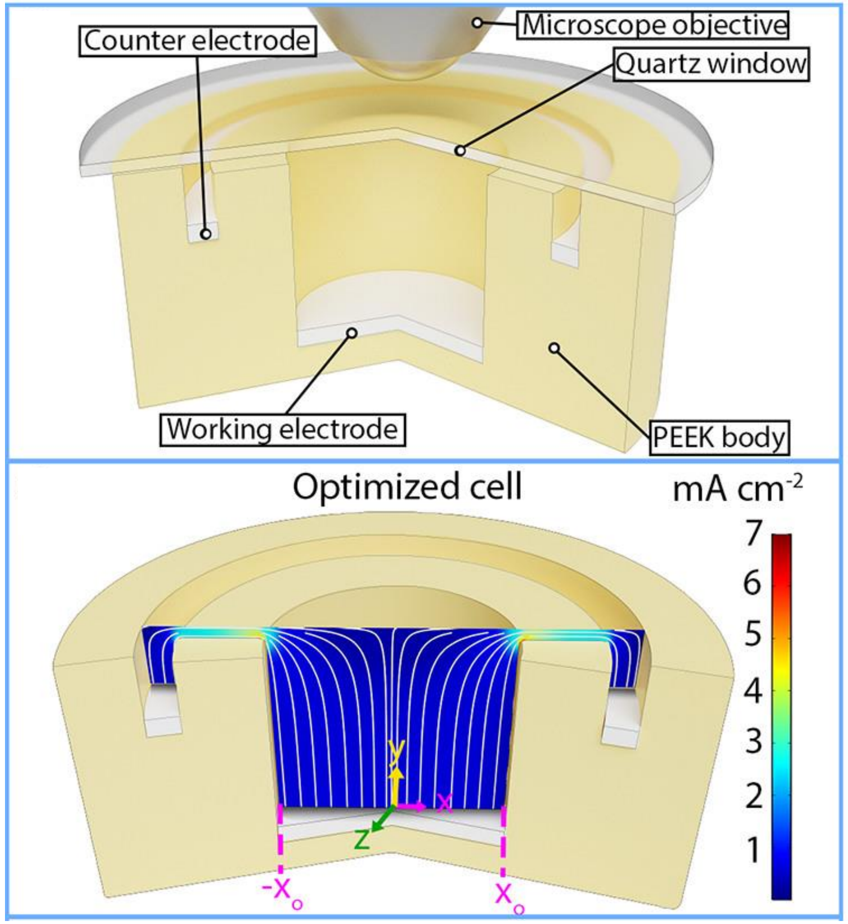


USABC XFC target

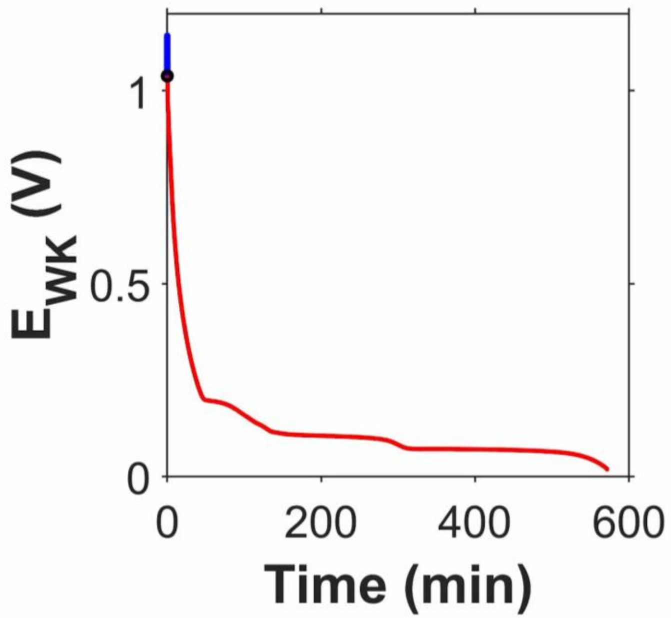


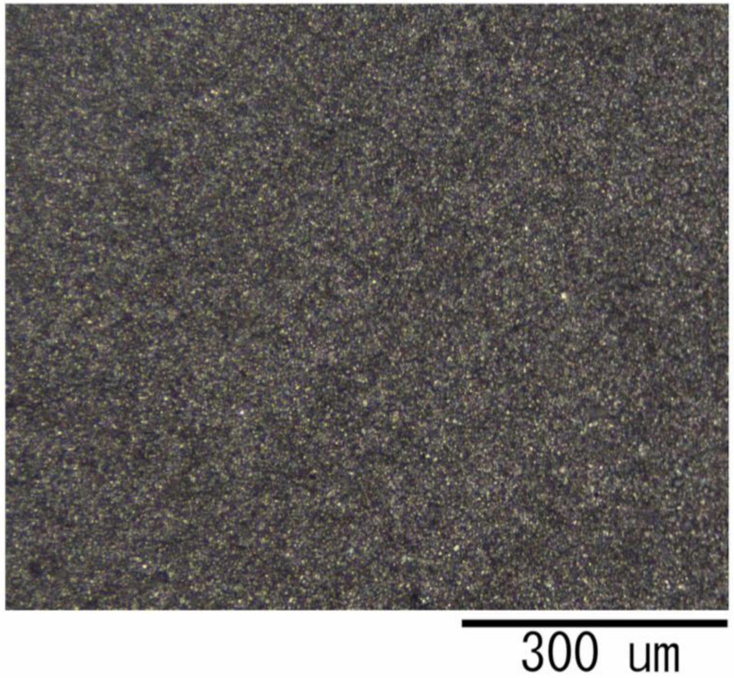
Accomplishment - *operando* video microscopy

- Use *operando* video microscopy platform to observe the onset of Li plating and the formation of "dead Li", and correlate these to electrochemical signatures (Milestone, Aug. 2019)



Slow charging



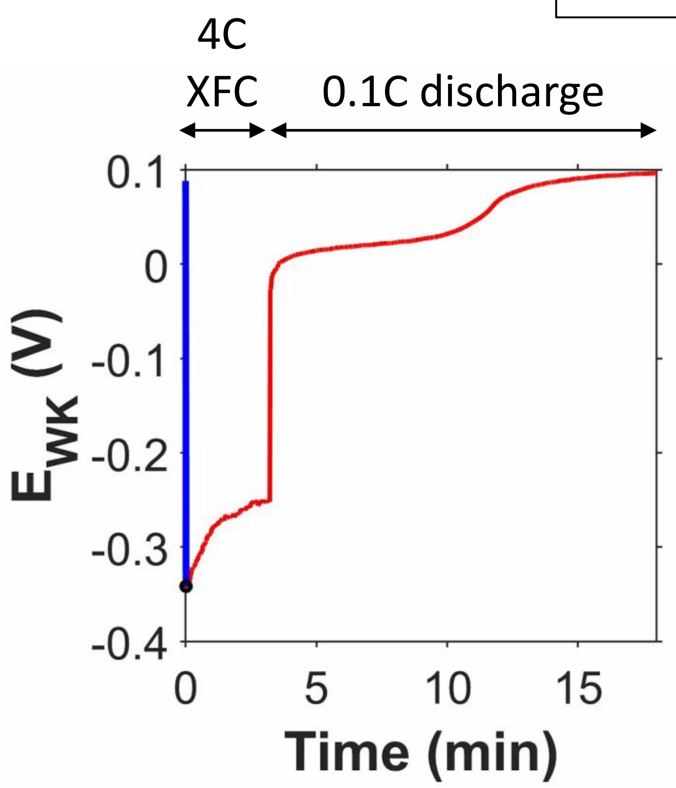


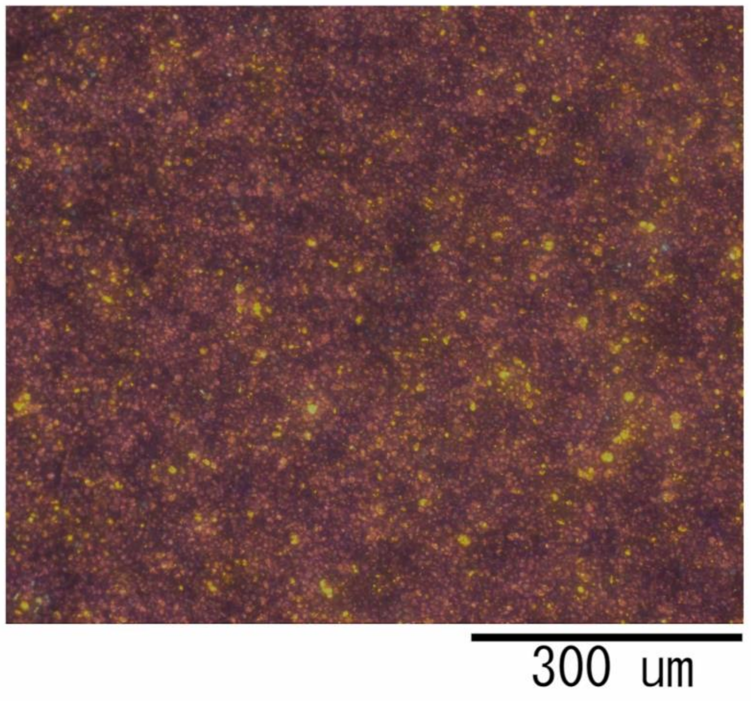
A.J. Sanchez, N.P. Dasgupta *et al. ACS Energy Lett.* **5**, 994 (2020)

Accomplishment - *operando* video microscopy

- Use *operando* video microscopy platform to observe the onset of Li plating and the formation of "dead Li", and correlate these to electrochemical signatures (Milestone, Aug. 2019)

4C Fast charging

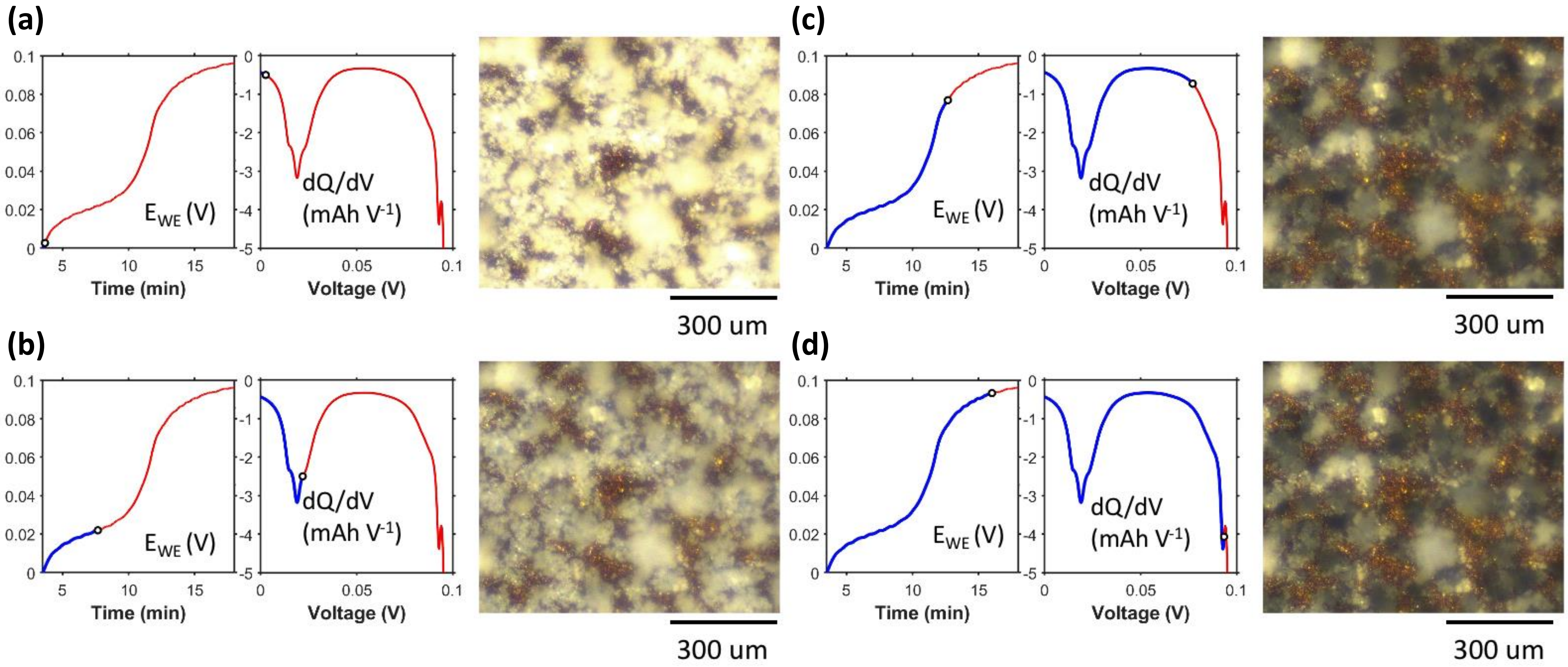




Accomplishment - *operando* video microscopy

- Use *operando* video microscopy platform to observe the onset of Li plating and the formation of "dead Li", and correlate these to electrochemical signatures (Milestone, Aug. 2019)

Li re-intercalation signature during early 0.1C discharge

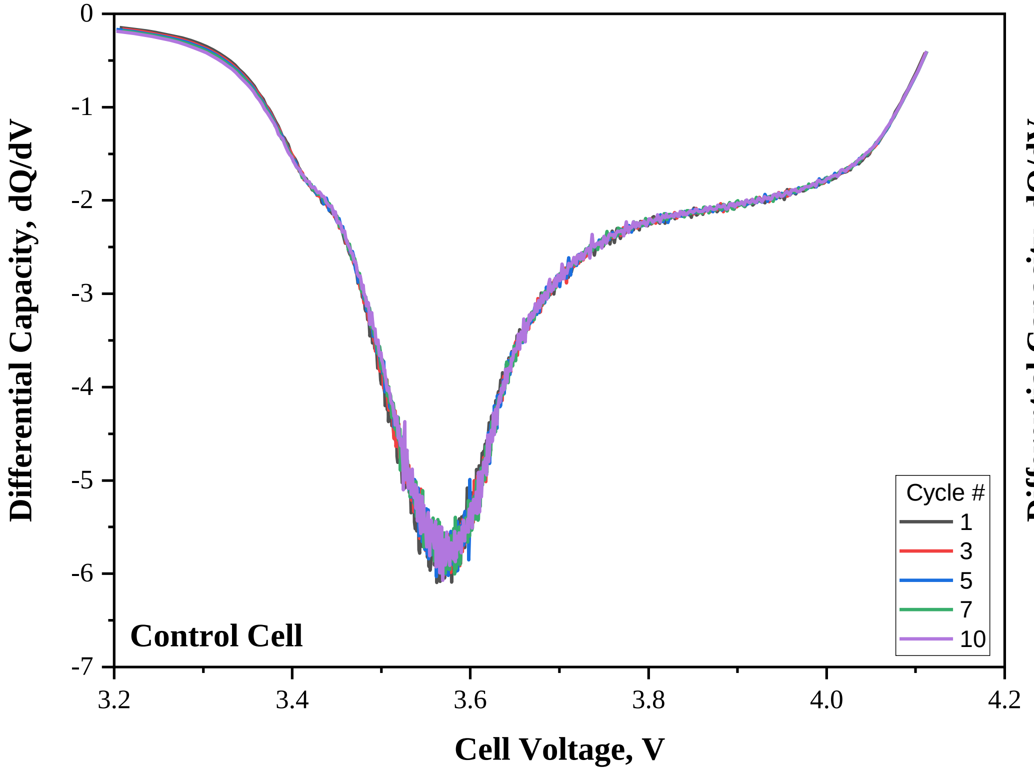


Accomplishment - dQ/dV analysis

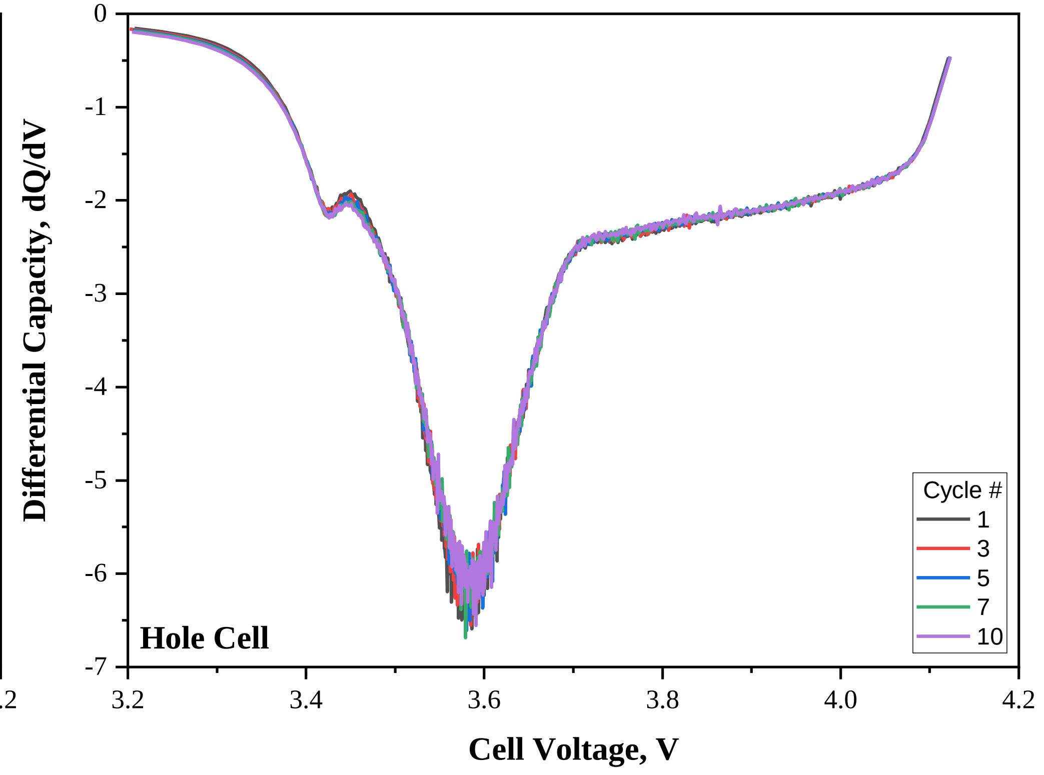
- Use high-precision Coulometry and dQ/dV analysis to detect Li plating signatures in the pouch cells during XFC (Milestone, May. 2020 – on schedule)

dQ/dV analysis on 0.5C discharge (after 0.5C charge)

Control



HOLE

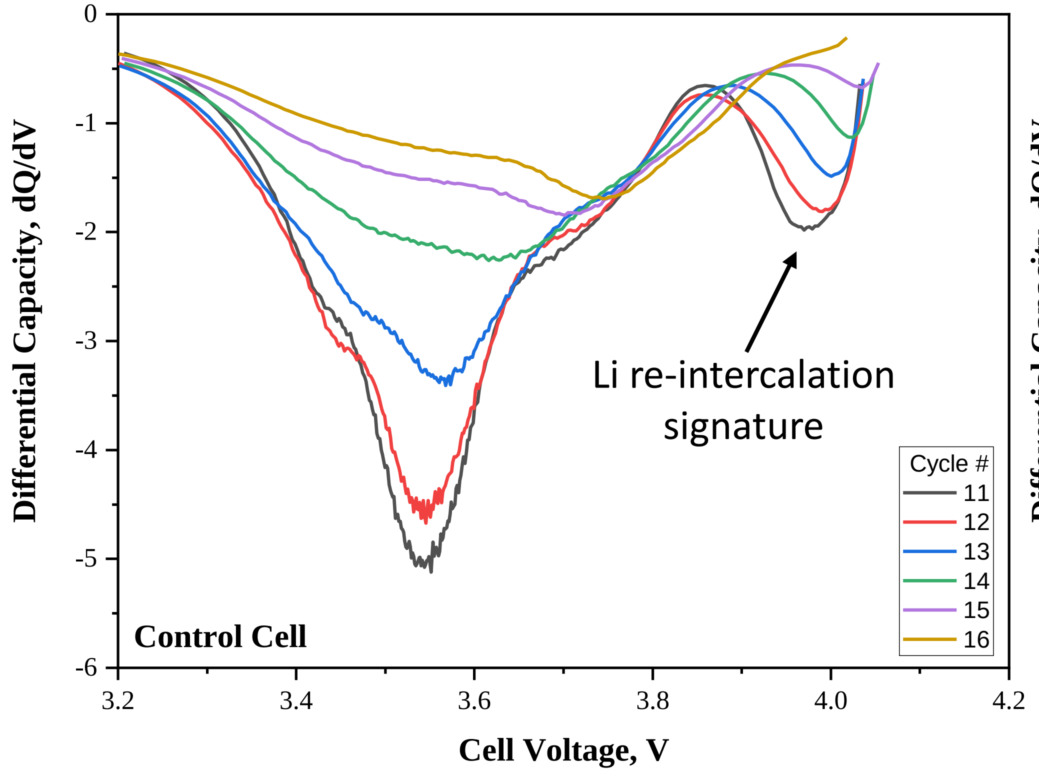


Accomplishment - dQ/dV analysis

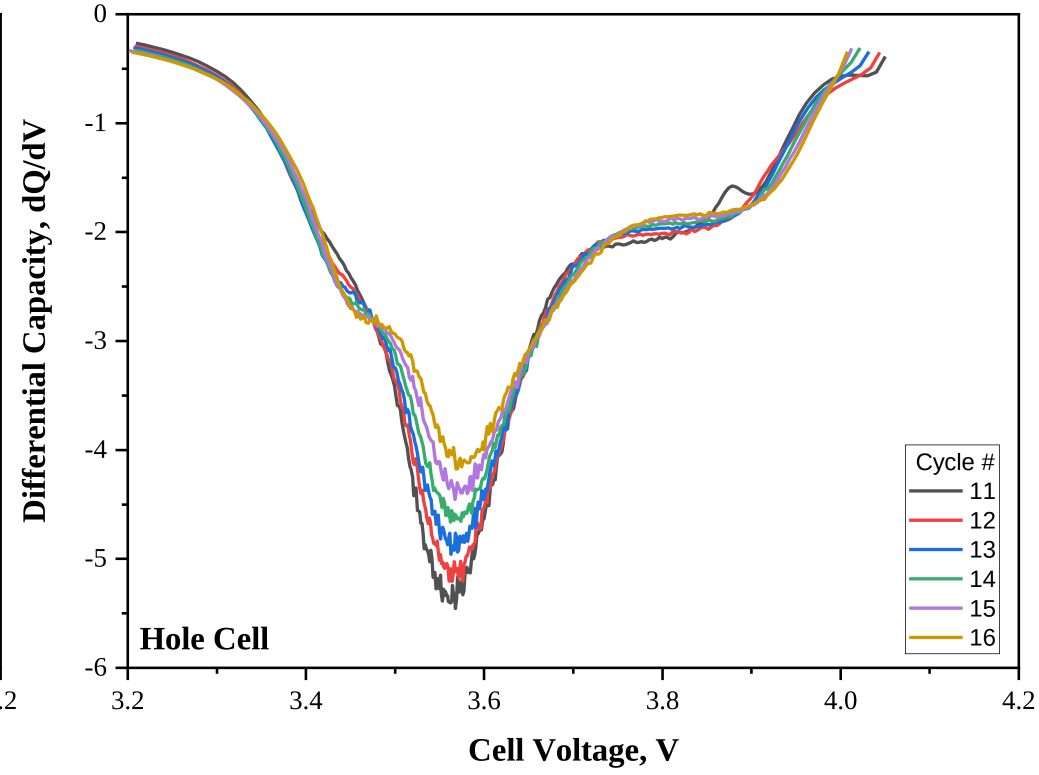
- Use high-precision Coulometry and dQ/dV analysis to detect Li plating signatures in the pouch cells during XFC (Milestone, May. 2020 – on schedule)

<u>dQ/dV analysis on 1C discharge (after 6C fast charging)</u>

Control

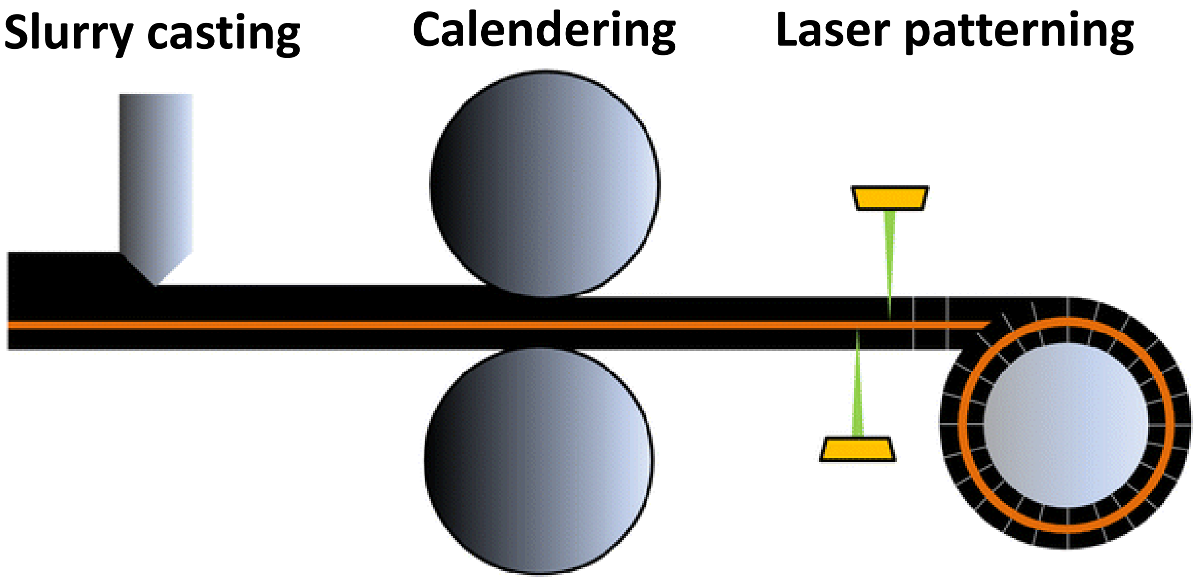


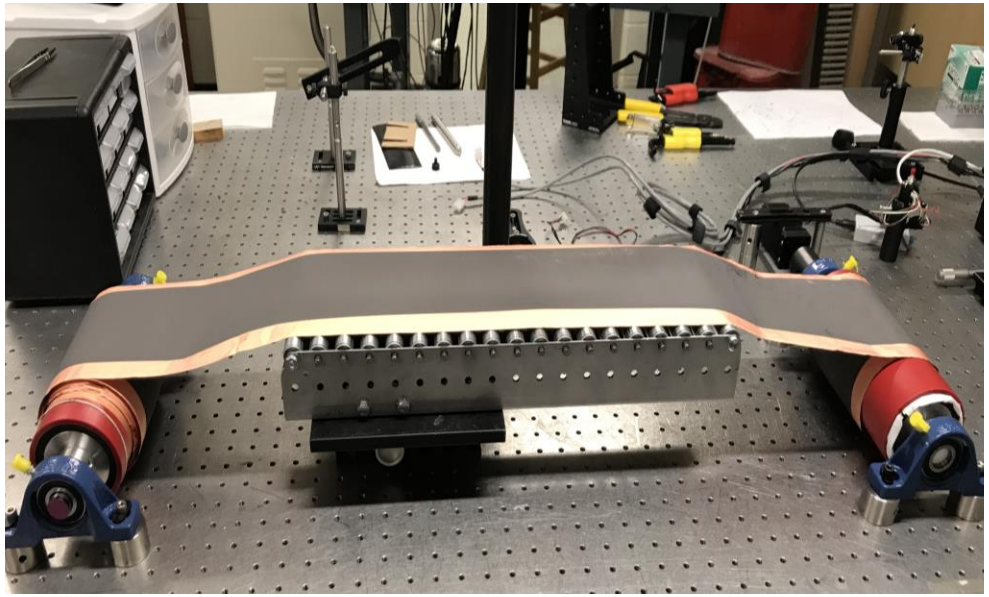
HOLE



Responses to Previous Year Reviewers’ comments

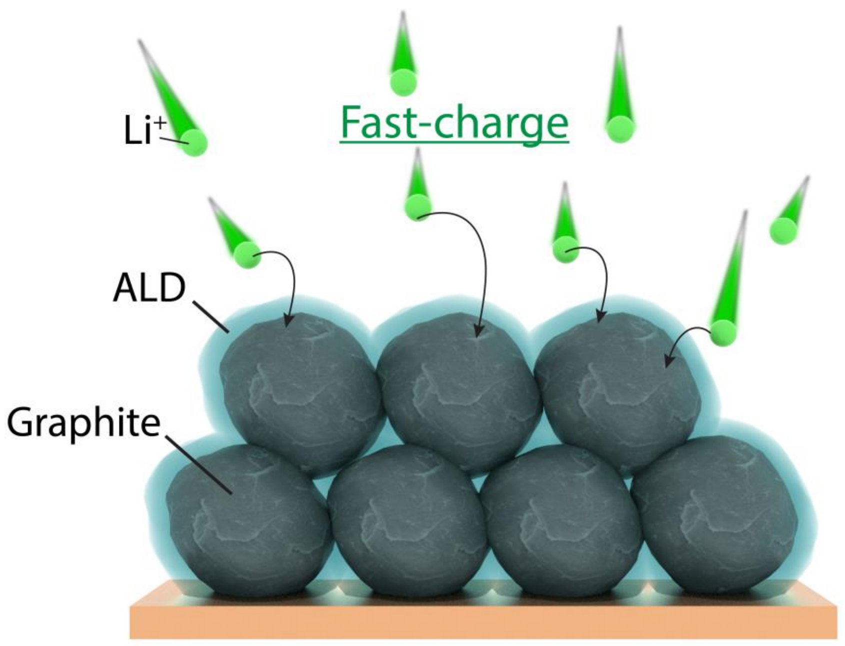
- **Increasing price and time due to the added laser processing should be quantified**
  - Laser patterning process is scalable and can be directly integrated into roll-to-roll lines
  - Lab-scale speed: 5,000 holes/s or 25 mm/min
  - Roll-to-roll (multi laser sources with beam splitters): 2.5 m/min
  - Calculated operating expenditure using the U.S. average electricity rate of 13.2 cents/kWh: 0.07 \$/m^2 anode or 0.45 \$/kWh

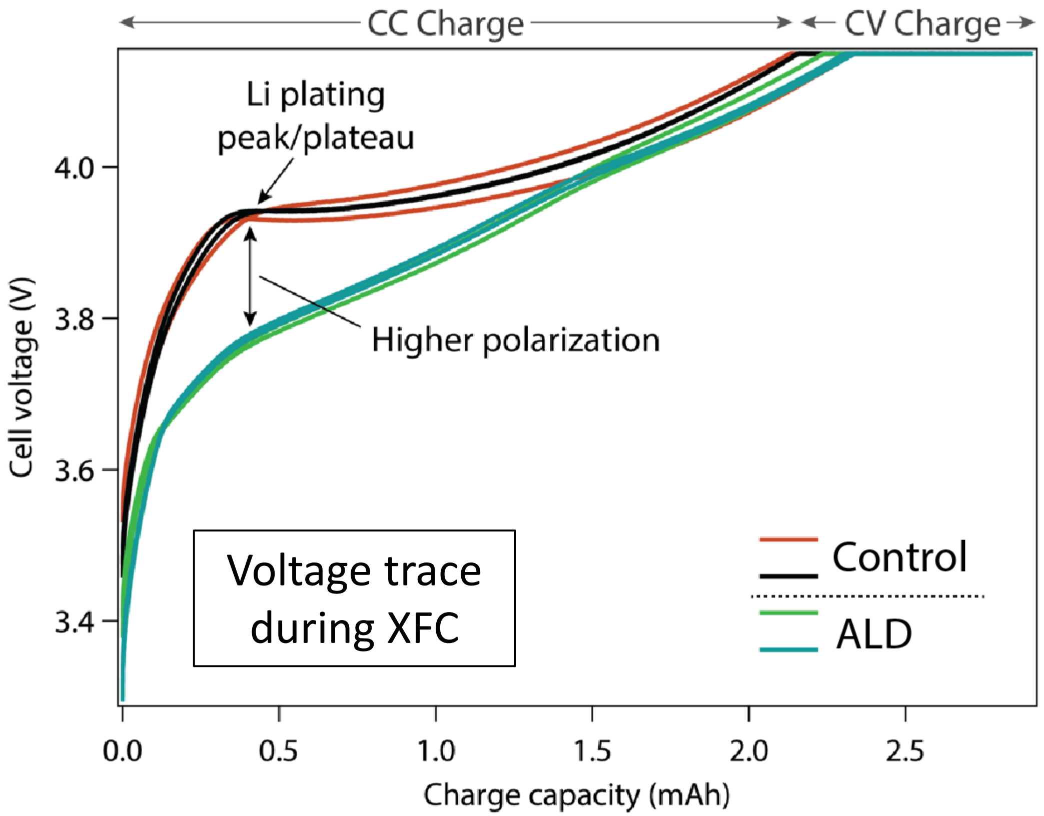




Responses to Previous Year Reviewers' comments

- **The reviewer did not see how the ALD treaments will help achieving improved XFC performance**
  - Demonstrated enhanced electrochemical performance during fast charging with ALD coatings on graphite anodes (Milestone, Nov. 2019)
  - Reduced cell polarization was observed for the ALD-treated anodes compared to the control

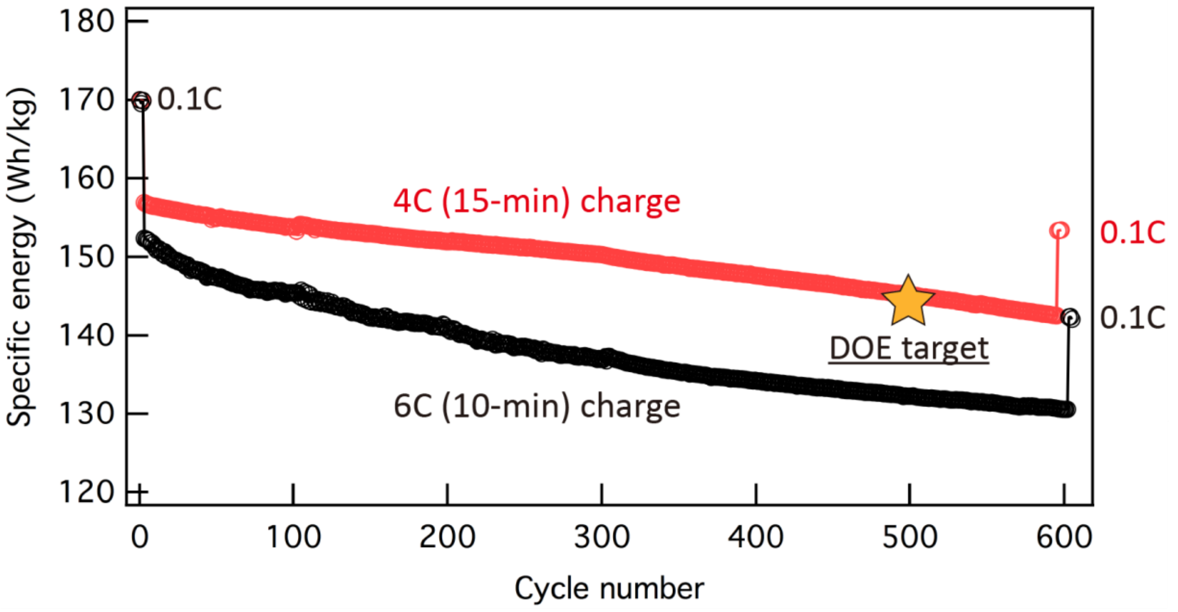




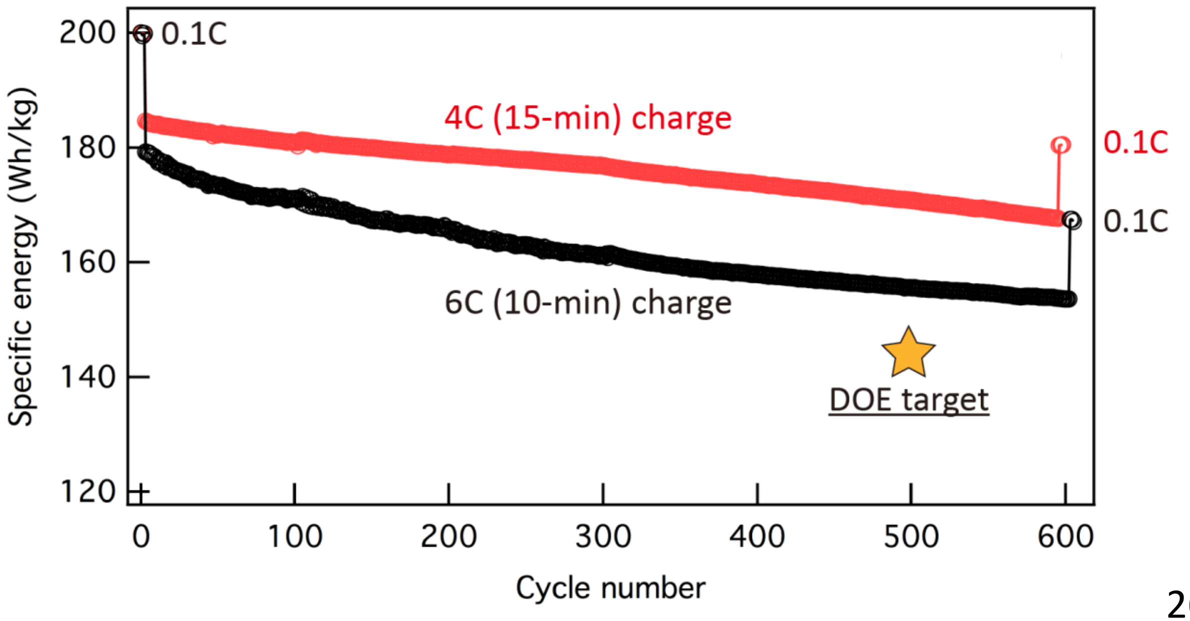
Responses to Previous Year Reviewers’ comments

- **Fast-charge goals of charging 80% SOC in 15 minutes and long-term cycling with < 20% capacity fade over 500 cycles need to be addressed**
  - Achieved these targets with the results summarized in slide 18
- **Energy density greater than 180 Wh/kg should be the key target to achieve XFC goals**
  - Addressed the gravimetric energy density target by scaling up to 20 Ah cells
  - Working on adopting high-energy cathodes and patterning > 3.5 mAh/cm^2 anodes

Current – 170 Wh/kg cell



Projected – 200 Wh/kg cell



Collaboration and Coordination with Other Institutions

Sandia National Lab – Josh Lamb, and Loraine Torres-Castro

- Leverage unique high precision Coulometry and Rapid EIS capabilities in the Battery Abuse Lab to identify electrochemical signatures of plating during XFC conditions

Argonne National Lab – Andrew Jansen

- Testing HOLE modification of XFC electrode manufactured at CAMP facility

SLAC National Accelerator Lab – Mike Toney

- *Operando* synchrotron XRD of HOLE electrodes during XFC

ETH Zürich – Prof. Vanessa Wood

- X-ray tomography of HOLE electrodes

Remaining Challenges and Barriers

- Additional characterizations on early Li plating markers during fast charging
- Mapping of chemical inhomogeneity in the electrolyte and at the electrode/electrolyte interfaces
- Delivering cells with > 180 Wh/kg at the beginning of XFC and > 144 Wh/kg (< 20% capacity fade) after 500 cycles of XFC
- Achieving industrially relevant processing speed with the laser patterning platform

Proposed Future Research

- Use high-precision Coulometry and Rapid EIS to generate Li plating markers (<u>Milestone, May 2020</u>)
- Confocal Raman scans of Control and HOLE anodes for current densities ranging from 1-10 mA/cm^2 (<u>Milestone, Aug. 2020</u>)
- Scale up to > 10 Ah pouch cells and/or use high-energy cathode materials to achieve required energy density (<u>Milestone, Aug. 2020</u>)
- Optimization of a prototype roll-to-roll laser patterning tool that enables high-throughput processing commensurate with a Li-ion coating line

Any proposed future work is subject to change based on funding levels

Summary

- Designed and constructed high-power laser platform capable of rapid and scalable modification of pouch-cell-sized electrodes
- Demonstrate laser patterned graphite anodes (> 3 mAh/cm^2) for fast charging Li-ion in > 2 Ah pouch cells
- Systematically investigated effect of HOLE anode design on rate capability and Li plating in graphite anodes, demonstrating significant improvement in XFC cycling and reduced Li plating
- Parameterized computational model informed by experimental results to simulate charge/discharge voltage curves and concentration gradients
- Performed high-precision Coulometry and dV/dQ analysis on pouch cells to detect Li plating signatures

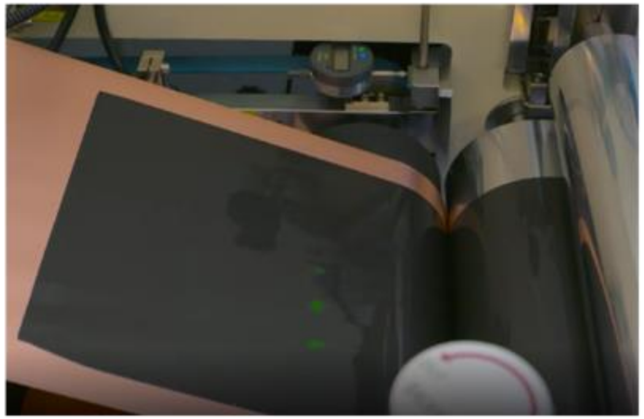
Technical Back-Up Divider Slide

Technical Back-Up Slide

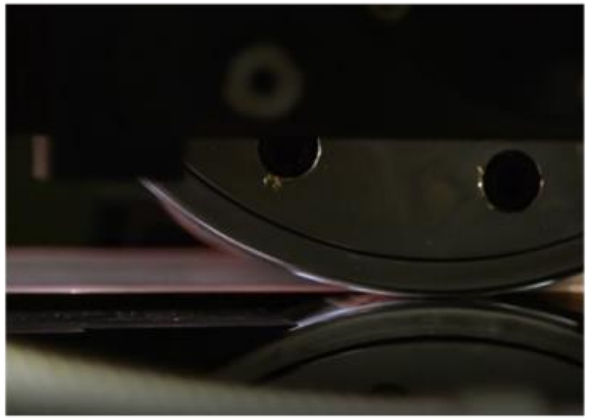
- Pouch cell fabrication and laser patterning processes

1) Powder/slurry mixing

2) Roll-to-roll electrode coating

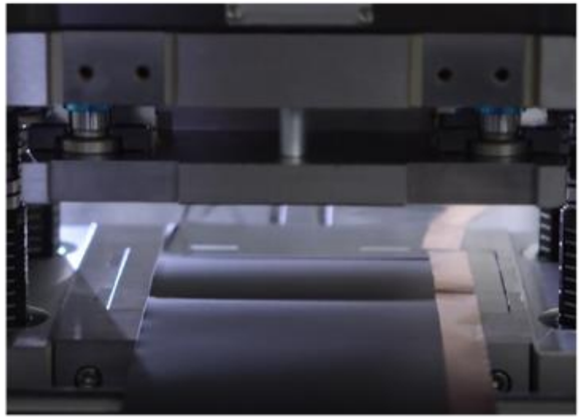


3) Calendering (roll pressing)



4) <u>Roll-to-roll Laser Patterning</u>

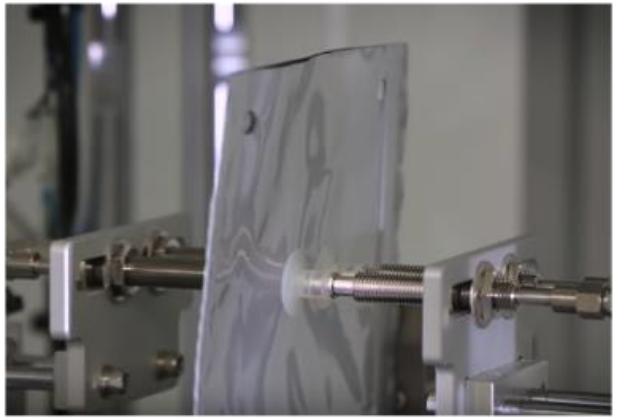
5) Electrode punching



6) Electrode stacking

7) Ultrasonic tab welding

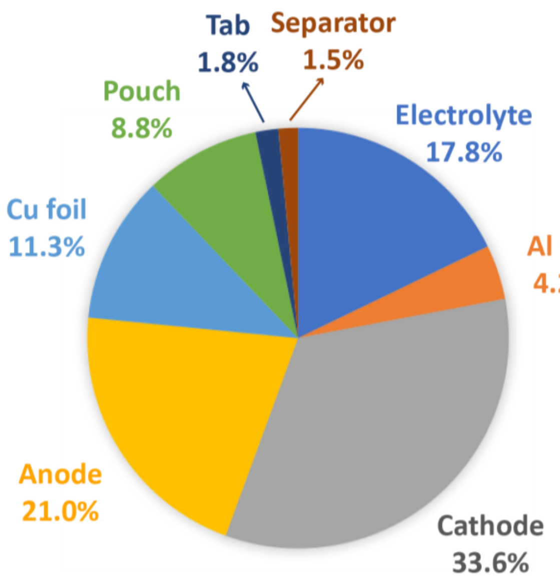
8) Electrolyte filling



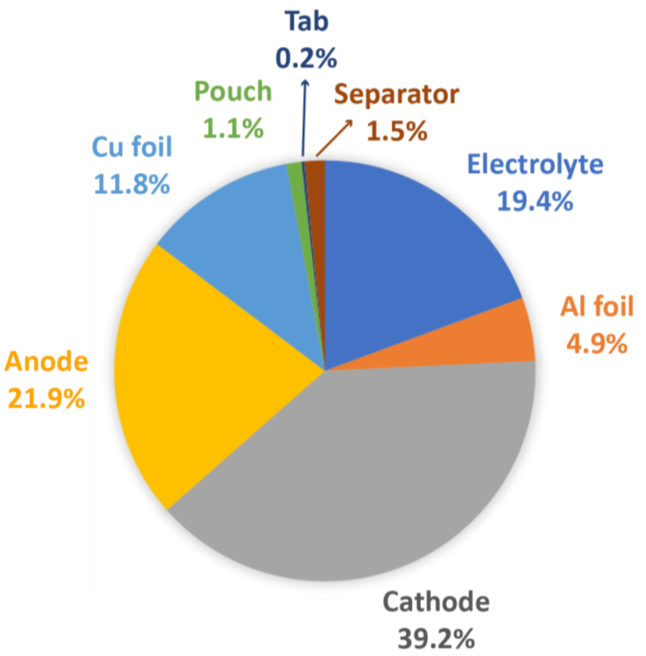
Technical Back-Up Slide

- Specific energy (Wh/kg) for the 2.2 Ah and 20 Ah HOLE cells

2.2 Ah HOLE cell
170 Wh/kg

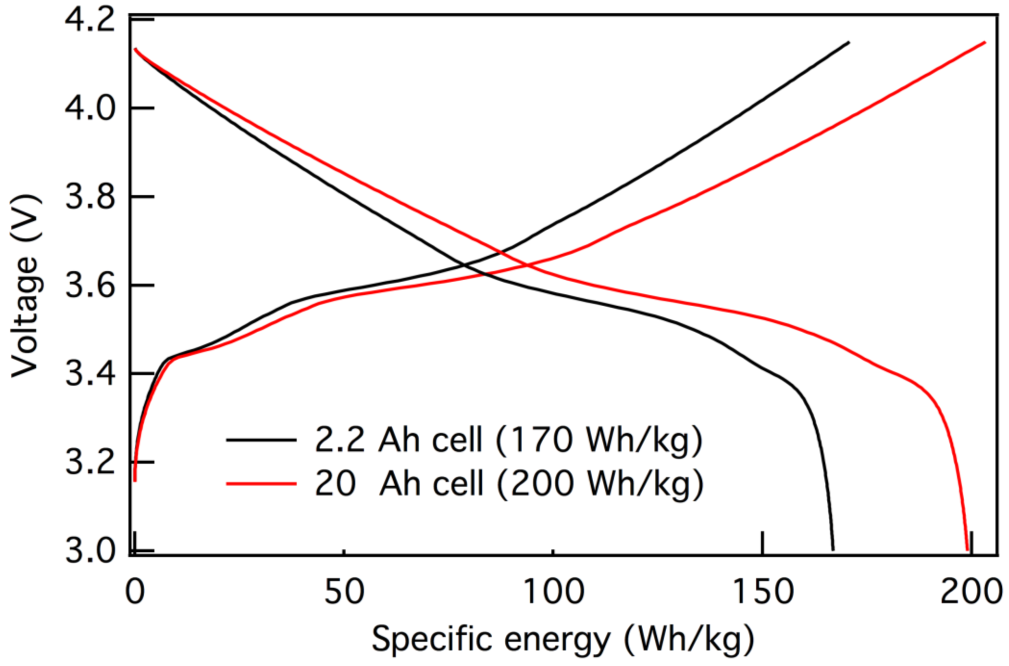


20 Ah HOLE cell
200 Wh/kg



Pie charts showing mass fraction of each cell component

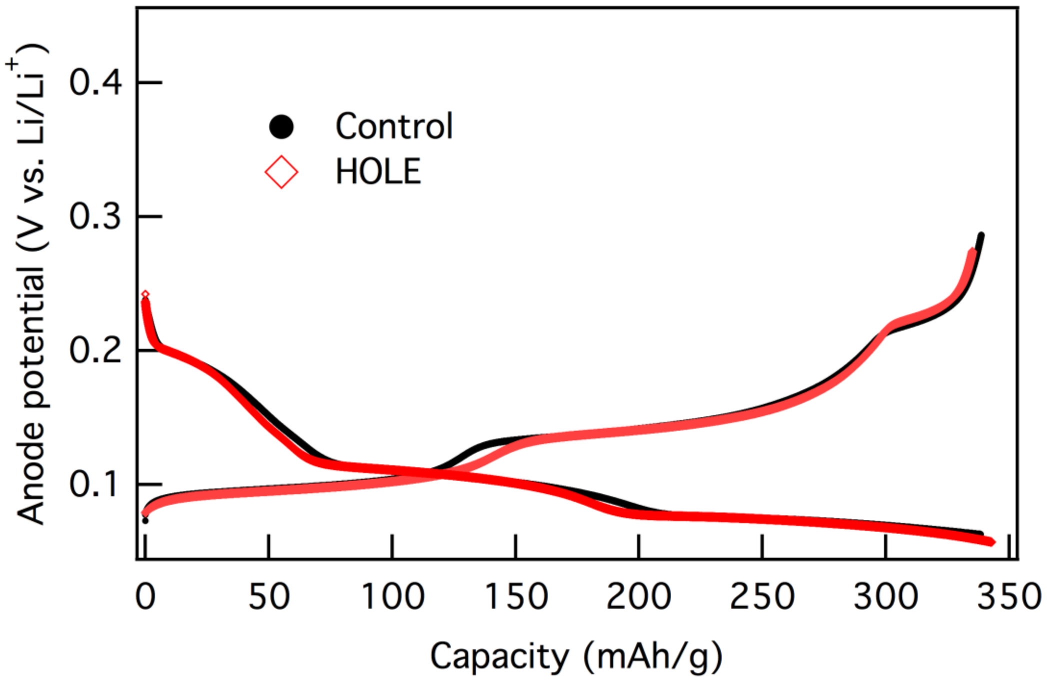
3.0 - 4.15 V cycling at C/10 rate



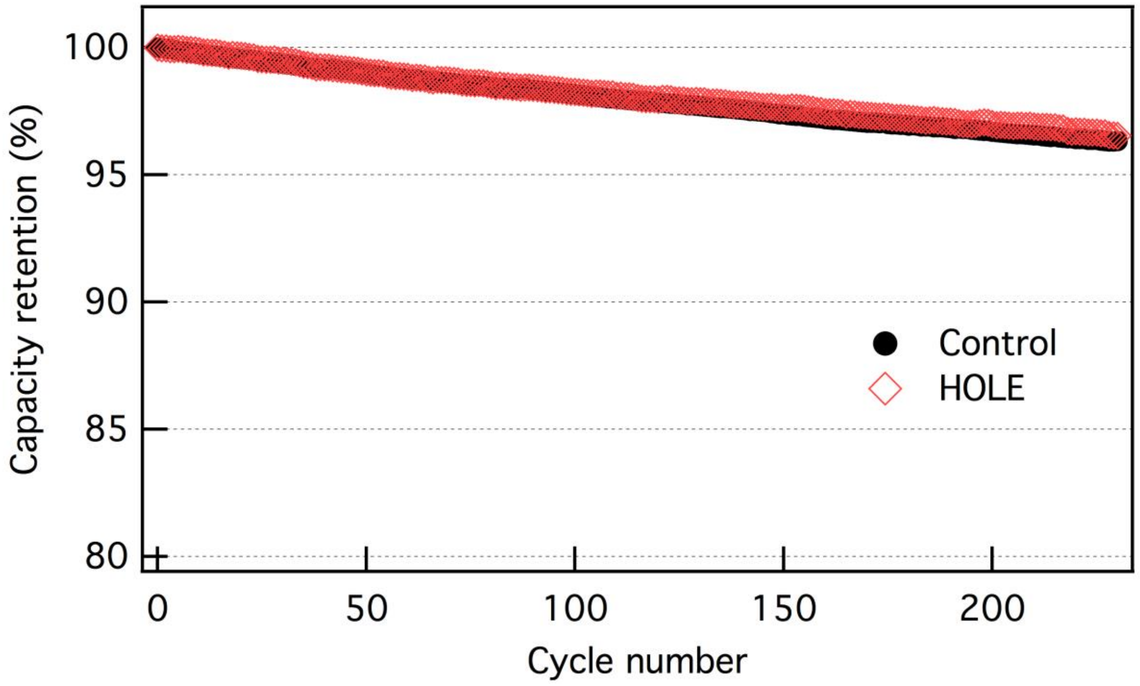
Technical Back-Up Slide

- Standard cycling performance of Control and HOLE cells
- Similar initial Coulombic efficiency (~88%) and specific capacity (~340 mAh/g) for both control and HOLE anodes
- Good standard 1C/1C charge/discharge cycling performance (aging rate ~1.5% fade/100 cycles)

Voltage profile

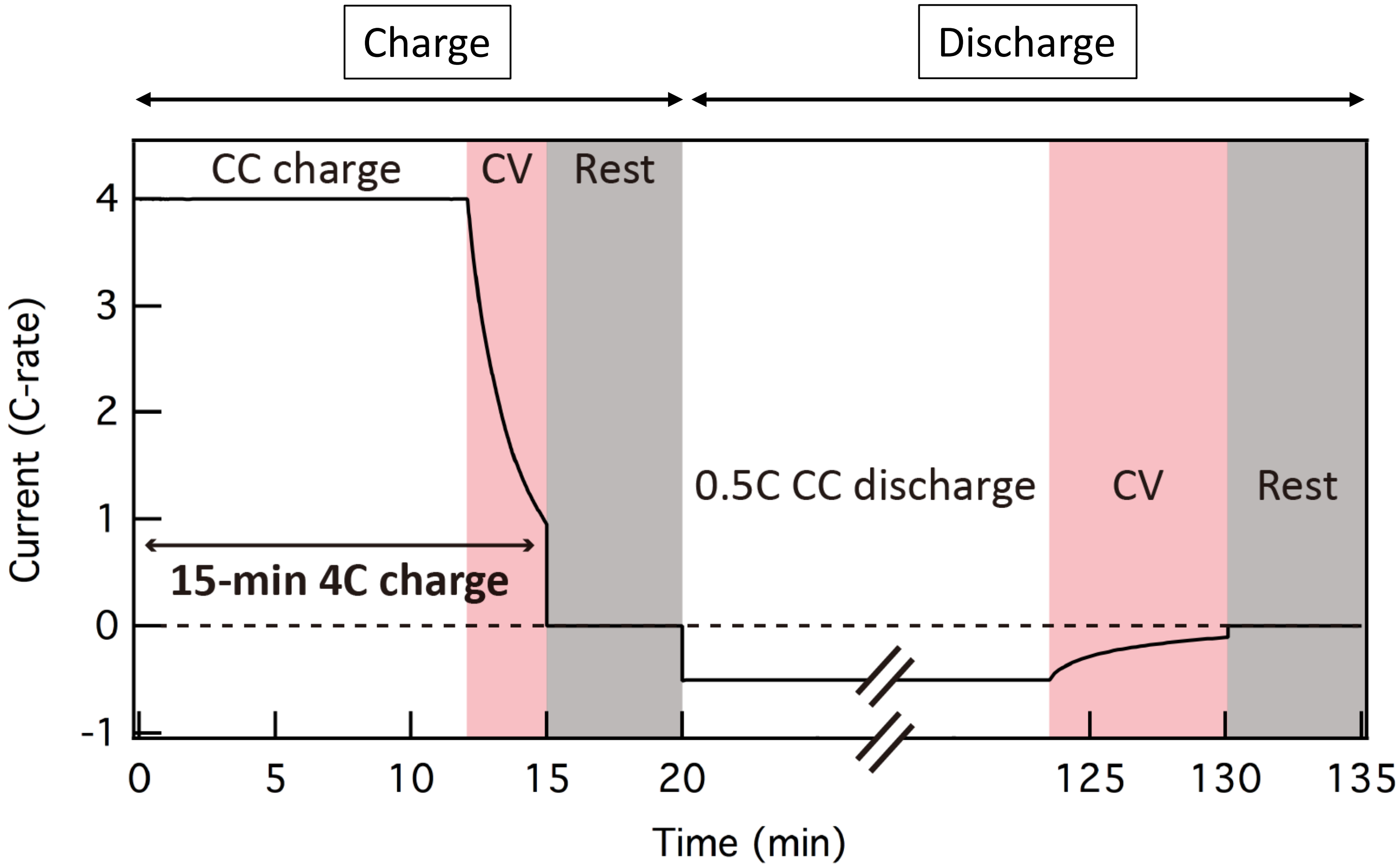


1C/1C charge/discharge



Technical Back-Up Slide

- Fast-charge cycling protocol
- <u>4C fast charge</u>: CC-CV charge until 15 min charge time
- <u>6C fast charge</u>: CC-CV charge until 10 min charge time



Technical Back-Up Slide

- A full cell model was developed using porous electrode theory
- Parameterize simulations based on 3-electrode experiments by adjusting effective ionic diffusivity in the electrolyte, effective solid-state diffusivity in graphite, and reaction rate constant
- Results show good agreements between the experimental and simulated voltage traces at varying C-rates (C/10 - 6C)